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THE SITE OF REACTION IN SOLID-STATE DIGESTION
A New Hypothesis

D. J. MARTIN

Department of Chemical and Environmental Sciences, University of Limerick, Ireland

The literature on solid-state digestion (SSD) reveals no convincing physical model of the process. Most of the reported reaction models implicitly assume homogeneity: the heterogeneous nature of the waste substrate may be noted but is rarely modelled. In contrast, this paper proposes an essential role for heterogeneity. A multi-zoned physical model and a localized reaction site are consistent with many characteristics of SSD.

The fundamental hypothesis is that methanogenesis requires sites protected from the rapid acidogenesis occurring in the richer elements of the waste. If this protection is provided by mass-transfer resistances within pockets of leaner material, it is essential that their identity is not destroyed by excessive mixing or size reduction. A possible mechanism for such an effect is furnished by the proposed model, with a central role for mass transfer. Reaction is envisaged as occurring only in a thin layer, at an interface between rich and lean material. Acetogenesis and methanogenesis take place in distinct zones, with the latter protected from acid inhibition by mass-transfer resistances in an intervening buffer zone. The rate of waste stabilization is determined by the rate of advance of this multi-zoned reaction front. Several of the mass transfer processes occurring between these zones could be rate-limiting.

This model suggests that methanogenesis in a typical landfill gradually spreads from discrete initiation points, with the reaction zones forming an expanding set of concentric shells. Process optimization may thus require maximizing the number of initiation points, subject to a constraint: only the larger seed fragments can develop. Reported failures to replicate the process at laboratory scale might thus be due to the use of homogenized feedstock. The implications of the model for commercial practice are discussed, as are potential methods of experimental verification.

Keywords: solid-state digestion; methane; waste; model; mass transfer; particle size.

INTRODUCTION

The biodegradation of solid wastes by anaerobic microbial metabolism is known by a variety of process titles. Table 1 shows the multiplicity of alternatives in recent publications, in contrast with the consensus for other biodegradation processes[1–18]. Standardization on the term Solid-State Digestion (SSD)[16] is recommended. This paper focuses on its simplest and most usual form, in which the waste at any point is added in one load then neither mixed nor irrigated, so that biodegradation takes place in a largely static bed. This will be referred to as Batch SSD (BSSD).

BSSD may be carried out in an engineered landfill or in a digester. In either case, the same biochemical and microbiological mechanisms apply as in classical Anaerobic Digestion (AD)[19–21] but the operating conditions differ greatly. Mass-transfer resistances are small in the slurries and solutions to which classical AD is restricted. They are further reduced by mixing, due to both biogas evolution and mechanical agitation. In the solid media of BSSD, however, these resistances are very much larger. Moreover, there is no mixing and the biogas escapes through voids, rarely disturbing the waste bed. Similarly, acid inhibition is minimized in AD by control of the feed rate, but is severe in BSSD, in which there can be no such control.

Despite these radical differences, much of the thinking on the digestion of solid wastes is based on laboratory-scale AD research using continuous stirred-tank reactors, with slurries or solutions as feedstock. In AD, with small particles and adequate mixing, the rate is unlikely to be limited by mass transfer. (In continuous AD, either hydrolysis or methanogenesis may be rate-limiting, depending on the substrate. In batch AD, methanogenesis is likely to be rate-limiting initially, then hydrolysis later.) However, in SSD, with much large particles and no mixing (or none at the molecular level), mass transfer may well be limiting. This is a crucial distinction. If, as argued below, the effects of poor mass-transfer, localized reaction and acid inhibition are central to SSD, studies of AD may be of little relevance.

These effects are reduced in some forms of SSD by mixing or irrigation. Both techniques assume a need to disperse methanogenic inocula and/or nutrients. These intuitive but unproven assumptions are therefore relevant to a consideration of the reaction mechanisms in BSSD.

Mixing is highly stimulatory and several full-scale mixed digesters are nearing a decade of operational experience[5,7,10,22,23]. However, the engineering needed to mix a

Table 1. Nomenclature in biodegradation processes.

	Aerobic metabolism	Anaerobic metabolism
Substrate as a solution, with or without fine suspended solids	Activated sludge process**	Anaerobic digestion**
Substrate as a thick suspension or slurry	Aerobic digestion*	Anaerobic digestion**
Substrate as moist solid, with flow	Accelerated composting* (with flow of air)	Flushing bioreactor** (with flow of recycled leachate)
Substrate as moist solid, in mixed or static bed	Composting**; accelerated composting* (with mixing)	Dry digestion[1,5]; two-phase anaerobic digestion[2]; anaerobic digestion[3]; high-solids anaerobic digestion[4]; semi-dry digestion[6,7]; wet digestion[8]; anaerobic decomposition[9]; anaerobic fermentation[10,18]; anaerobic solid-state fermentation[11,12]; anaerobic composting[13–15]; solid-state digestion[16]; batch solid-state digestion[16]; anaerobic batch degradation[17].

* Conventional process titles are marked by double asterisks, while other widely used titles are marked by single asterisks. Note the contrasting diversity of titles for essentially similar solid-state digestion processes. Most of those cited were used in a single conference in 1999.

bed of irregular solids imposes high capital and operating costs. Consequently, most of these plants have been built under subsidy schemes[24].

Irrigated SSD (ISSD) is also effective[9,25,26]. It is also cheaper than mixing and, like BSSD, can be adapted to either a digester or a landfill. This 'flushing bioreactor' concept is usually realized by operating at high moisture content and recycling the leachate. An underlying principle is that of synchronizing the multitude of localized processes by harmonizing conditions throughout the waste. Although it will be argued below that true synchrony may be neither attainable nor desirable, there is no doubt that irrigation is initially stimulatory. The pre-methanogenic lag is considerably shortened and a high biogas output is quickly attained, although usually with rapid, wide fluctuations of rate. As the rate from large test cells seems as variable as it is at bench scale[27–30], the output at site scale might be equally unstable. This would reduce the economic viability of gas utilization, a problem that does not seem to have been addressed. Other doubts about the practicability of the flushing bioreactor at large scale include the risks of leachate leakage and maldistribution. These are well reviewed in a recent report, which proposes an extended trial at site scale. The authors argue that previous research, typically funded for only a few years, could never have delivered a full picture of the process[31]. Commercial viability has been predicted[32], so this proposal seems well justified.

Pending proof of this concept, BSSD in landfills will remain the most common form of SSD. It occurs naturally in most landfills, which remain the dominant means of waste disposal outside Europe. Even within the EU, under the recent Landfill Directive, it will be many years before the input of organic matter to landfills is eliminated. The application of standard methodologies[33] can show landfill to be the Best Practicable Environmental Option and the waste management industry in some countries has long experience with well-engineered and well-managed sites. A mass of operational data has been accumulated, from normal operation and from research projects based on test cells, both with and without leachate recycle[29,34–39]. This shows that good containment of pollutants can be attained but that rates of waste stabilization can vary widely. This poses questions as to the long-term maintenance of containment and thus of sustainability. Process acceleration would minimize such risks, in addition to the more obvious economic advantages, which might make BSSD competitive with ISSD.

The most pertinent of this operational data includes the following observations.

(a) Samples excavated from old landfills vary widely. In some areas the waste has been fully biodegraded, while in others, maybe decades old, the waste has barely changed. Newspaper has been reported as legible, while some food looks 'good enough to eat'; its smell was not recorded! Such process failures are often attributed to local acidification, perhaps due to inhibitory industrial wastes or high concentrations of food wastes[9,26,27,40].
(b) It follows that the effective rate of biodegradation is highly variable. Some parts of a landfill progress to active methanogenesis within weeks of placement of the waste, others take years to reach the same stage. This observation, like (a), might suggest that BSSD is an inherently unpredictable process, highly sensitive to operating conditions and commonly on the brink of failure. However, it is suggested below that this is due to severely sub-optimal seeding in most landfills.
(c) Free moisture is essential. High levels appear to be beneficial[37,39,41], while biodegradation almost ceases at moderate levels. This led to the unsustainable 'dry tomb' concept in landfill design, now discredited, in which capping excluded rain and the natural moisture content of the waste was too low for SSD[26,34,41,42]. The effects of flooding, at the other extreme, are less clear. Operation of a flushing bioreactor in upflow mode has been advocated[31] but flooding may not always be beneficial without flow[43,44].

(d) Irrigation is highly stimulatory too. It is assumed to promote mass transfer, distributing the inoculum and evening out any local shortages of nutrient or excesses of toxins or inhibitors[28]. The regulation of moisture movement has therefore been widely studied, partly because few other conditions can be controlled at site scale[31].
(e) Waste density is important. Compression to give a high bulk density not only conserves site capacity but also stimulates degradation. A possible mechanism is suggested below. However, the low final permeability of compressed waste might prevent the flushing of soluble by-products needed for full stabilization[44–46].
(f) Shredding and seeding would be expected to accelerate biodegradation but there is no clear evidence that they always do, despite many trials[35,55,57–67]. Both concepts are discussed further below.
(g) Biogas production rises slowly to a broad peak, typically over several years, then declines slowly, typically over several decades. Many attempts have been made to apply first-order decay kinetics to the deceleration phase but the fit is often poor[47].

Few process models have directly addressed the connections between reaction, inhibition, heterogeneity and mass transfer in SSD. Indeed, many reaction models pay little attention to the physical nature of the substrate. Either homogeneity is assumed or heterogeneity is acknowledged but not modelled. (A recent exception[11] will be discussed later.) Other models focus on thermal effects or on the movement of moisture or gases[30,48,49]. Significantly, many models apply only within a restricted range of scales[50]. This suggests the omission of essential factors. It will be argued below that reaction and mass-transfer (of substrates and products, including inhibitors) are intimately related. Consequently, models that treat these phenomena as separate may not be capable of describing BSSD adequately.

The present work developed from an experimental study in which an unexpectedly high rate of biodegradation was attained without leachate recycle[51,52]. The results suggested that mass transfer process are critical and that seed particles below a minimum size are ineffective[53]. A new physical model of the SSD process is suggested here as a working hypothesis for the mechanisms involved.

PROPOSED MODEL

Some definitions are needed before discussion of the model, which is shown in Figures 1 and 2.

(a) The waste is categorized into two fractions. A rich fraction comprises the readily biodegradable fraction of the raw waste (e.g. foodstuff). The remaining lean fraction may include any of five components: recalcitrant material (e.g. paper, which degrades only slowly), depleted waste (approaching stability), stabilized waste, seed material and inert material. These may be separate or intermingled: the model applies to both sorted and unsorted wastes. The defining feature is that such materials cannot sustain rapid acidogenesis so can provide 'safe havens' for methanogenesis. For simplicity, this discussion assumes that the lean phase consists only of stabilized waste, serving as seed material.
(b) The overall reaction is considered as comprising two steps, acetogenesis and methanogenesis. The term acetogenesis is used here as shorthand for the reaction sequence hydrolysis-acidogenesis-acetogenesis, which is generally assumed rate-controlling[54]. The individual steps are distinguished only when necessary.
(c) Particles are referred to as 'fragments', for reasons to be explained later.
(d) The term 'seed' has been used for all materials used as sources of methanogenic bacteria, such as digested sewage sludge or previously-digested waste, to distinguish them from the true inocula, (microbial cells and spores).
(e) Planar geometry is depicted, to simplify description. A horizontal layer of homogenous rich material is shown lying above a homogenous lean layer. The figure is bounded above and below by the central plane of each layer, so a succession of mirror images can be conceived as extending vertically, through a multiplicity of similar layers. The plotted dimension 'Distance' is measured perpendicular to the interface, which is taken as an arbitrary datum.
(f) The figure is not to scale: Zones A and F are thick, while B-E, the relative thicknesses of which are unknown, might all be extremely thin.
(g) The model describes the process at micro-scale, as reaction proceeds *within* a fragment of waste. Thus, neither leachate recycle and nor liquid-phase transport mechanisms (convective or diffusive) are relevant.

The basis of the model is the solid curve shown in Figure 1, which represents the assumed volatile fatty acid concentration soon after the start of digestion. Rapid acidogenesis has raised the acidity in the bulk of the rich layer to inhibitory levels. (This step is described below as 'ensiling' by analogy with the similar method of crop preservation.) However, methanogenesis has begun in the depths of the lean layer, protected by mass-transfer resistances. Six reaction zones, some of which could be further sub-divided, are distinguished in the resulting concentration profile.

A. Ensiled zone. This consists of acidified waste, in which acetogenesis is prevented by acid inhibition. It is metastable (indefinitely stable, if anaerobic conditions are maintained) and extends for a considerable depth.

B. Inhibited acetogenesis zone. The acidity is slightly lower here, due to diffusion of acids into Zone C, so reaction can proceed—but under acid inhibition. The acidity gradient is shallow: mass-transfer considerations require a small change in acid concentration across the zone at steady-state, so inhibition is severe throughout this zone. Either hydrolysis, which also occurs here, or acetogenesis could be rate-limiting; the intermediate step of acidogenesis is known to be faster. Acid inhibition seems most likely to be the retarding factor. (However, a limit on the rate of hydrolysis could also be due to the availability of extracellular hydrolases. If secreted throughout the waste during the ensiling stage, they might still be present in the waste. However, such long-term stability is unlikely. More probably, any reaction in the upper regions of Zone B utilizes enzymes diffusing from below, probably from the lower levels of the same zone.) The thickness of Zone B is determined by completion of the conversion of the readily biodegradable fraction to acetate.

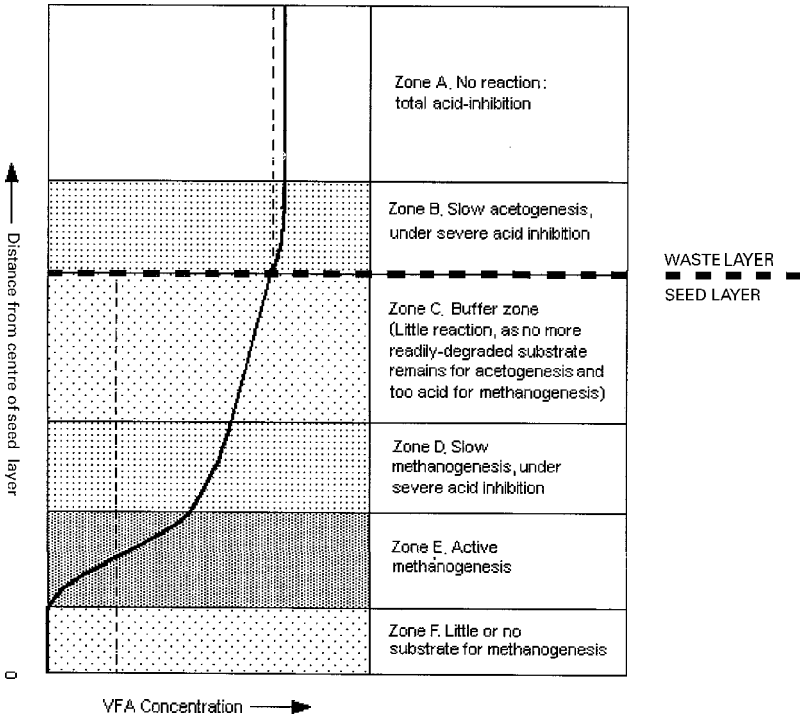

Figure 1. Initial location of reaction zones and concentrations of volatile fatty acids. (The B:C interface initially coincides with the surface of the seed. Solid curve: the VFA profile for the proposed micro-reactor model. Broken line: the VFA profile inferred from the model of Kalyuzhni *et al.*[11]. Shading as in Figure 2.)

C. Buffer zone. This passive zone consists of lean material, so can only form initially in a seed fragment. The acidity here is too high for methanogenesis, while there is little substrate for acetogenesis. Its depth is determined by the steepness of the concentration gradient and thus by the diffusion rate: the faster the acids diffuse, the greater the depth required to protect the methanogenic zones below. The linear gradient shown here applies only in planar geometry and is understated, for clarity; a much steeper gradient is expected in reality.

D. Inhibited methanogenesis zone. Methanogenesis begins here, utilizing acids diffusing from the buffer zone but the rate is depressed by acid inhibition.

E. Uninhibited methanogenesis zone. Methanogenesis reaches its (low) maximum rate. As in Zone D, most of the substrate is supplied by diffusion from the upper zones, so the reaction rate might be subject to a mass-transfer limitation. The thickness of Zone E is determined by the reaction volume needed to fully utilize the acids diffusing through Zones C and D.

F. Depleted zone. The rate of methanogenesis is very low here, due to substrate deficiency. All the acids generated in Zone B are consumed in Zones D and E, so the rate in this zone is limited by the local rate of hydrolysis. This is low because only the recalcitrant substrates remain. Methanogenesis can therefore utilize the acids as fast as they are produced, so the acid concentration is negligible. Reaction is therefore dispersed throughout this zone, which could be very deep, like Zone A. (This dispersed reaction commences in Zones B-E but its progress there is limited by the confined volume and acidity.) The deepest areas of Zone F consist of fully stabilized waste, in which no further digestion occurs.

This model suggests that the reaction zones are mobile, as shown in Figure 2. The substrates for acetogenesis in the original Zone B are gradually consumed, so the acid concentration falls, due to diffusion into Zone C. This allows acids to diffuse in from Zone A, lowering the concentration near the A:B interface. This reduces the degree of acid inhibition, so the acetogenic zone gradually creeps upward, followed by the buffer zone and, in turn, the two methanogenic zones. Biodegradation of readily-degraded substances thus approaches completion in a localized reaction front. This slowly advances from the seed phase into the waste phase, leaving behind it a growing depth of depleted waste. A dispersed residual reaction in the latter completes the process of stabilization.

Several distinct transport processes could be rate-limiting, rather than microbial metabolism or extracellular hydrolysis, as is usually assumed. Microbial growth no doubt occurs but might not result directly in process acceleration; growth might do no more than advance the reaction front. Other possible causes of process acceleration are discussed below.

DISCUSSION

The proposed model might explain the deficiencies of first-order process models[47], including their scale limitations[50], since the physical model underlying these is essentially homogeneous. Rates of biodegradation may depend on particle size in both waste and seed phases and on seed distribution, as well as on the variables commonly taken into account, such as temperature and moisture.

No comparable physical model of SSD appears to have been suggested before, although the role of heterogeneity has been noted. Barlaz *et al.* pointed out that acids must diffuse to the sites of methanogenesis[9] but described this as a 'physical impediment'[55]. A diffusive step might

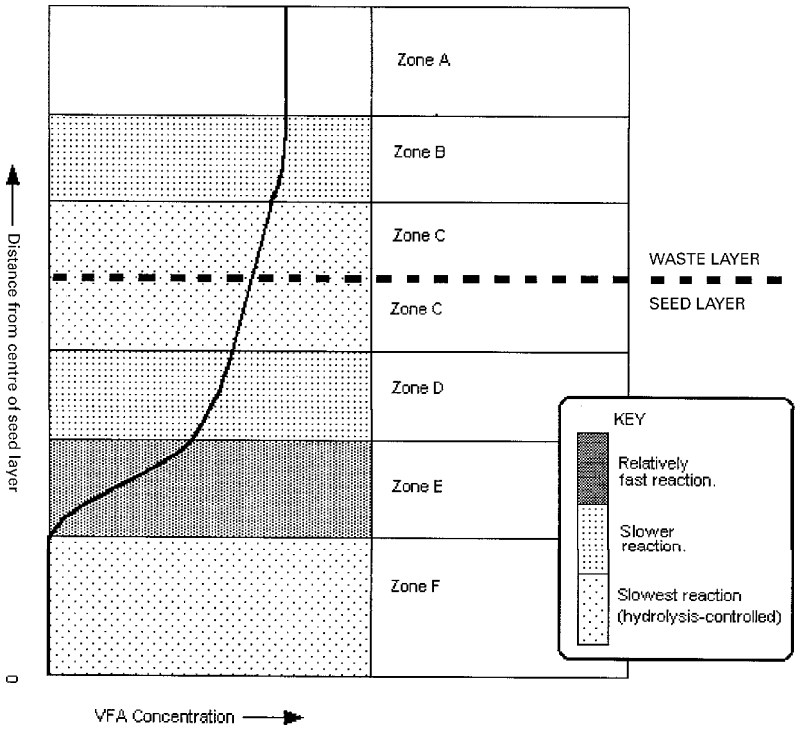

Figure 2. Location of reaction zones a short time later. (Reaction zones advancing into the waste fragment.)

indeed be rate-limiting but, as noted above, this impediment might be essential for process viability. Several authors have also suggested that moisture and inerts might helpfully 'dilute' the products of rapid acidogenesis in the richer wastes[27,40,56]. However, any such dilution might simply prolong acidogenesis, until inhibitory acid levels were also reached in the diluent. Inclusion of any diluent would therefore be ineffective.

In contrast, a large fragment of methanogen-rich seed material[53] could establish itself as an independent 'micro-reactor'—but the mechanism here is not dilution. In a large enough particle, well-populated with methanogens, a core zone will be surrounded by a buffer zone thick enough to protect the core from excessive acidity. If the methanogens in the core can metabolize acids as fast as they diffuse in, a quasi-steady state micro-reactor forms. This can only happen in a seed particle large enough to accommodate *both* a buffer zone thick enough to provide adequate mass-transfer resistance and a methanogenic core of adequate assimilative capacity. There is thus a minimum viable size of seed particle[53].

A lag phase is observed while these micro-reactors are forming. The process then progresses by their expansion into the waste, as the reaction zones advance *within* the waste fragments. This concept of expanding micro-reactors may be contrasted with 'shrinking core' models, in which the digestion of a waste particle is assumed to commence with external attack by hydrolases in the interstitial liquor.

This micro-reactor model suggests that the SSD process is inherently both asynchronous and heterogeneous at the scale of the reaction front. Consequently, models based on synchrony and homogeneity are unlikely to fit. Moreover, attempts to force SSD to conform to such models by fine shredding, mixing or irrigation may be futile or even counter-productive.

The recent 'two-particle' model of Kalyuzhnyi, Veeken and Hamelers[11] has some similarities to this approach, allowing for heterogeneity and for the links between reaction and mass transfer. However, the underlying physical model is quite different from that shown in Figure 1. Its basis is a substrate-rich waste fragment in contact with a lean seed fragment, into which the substrate diffuses. Both the seed and waste fragments are assumed 'well mixed', so reaction occurs uniformly throughout each particle. This implies a zero internal concentration gradient, with a step change at the interface. (Figure 1 includes, for comparison, a broken line representing such a concentration profile, with arbitrary values.) This leads to a single, inaccurate, diffusion equation in a complex 26-equation process model. The authors do acknowledge that their physical model is a simplification. However, if the micro-reactor model is correct, with its complex interactions between mass transfer and reaction, the value of linking sophisticated reaction models to simple physical models might be limited.

Development of a mathematical model of BSSD based on the micro-reactor model might be expected to be difficult, perhaps requiring the addition of several complex diffusion equations to the 25-equation reaction model proposed by Kalyuzhnyi, Veeken and Hamelers.

Moreover, the starting point is uncertain. A score of distinct mass-transfer steps could be rate-limiting: diffusion of acids through each of Zones B-E; diffusion of nutrients through the same four zones; diffusion of metabolic intermediates through the same zones (in both directions); diffusion of hydrolases towards the A:B interface; diffusion of soluble gaseous products towards the liquid-gas interface; transfer of gaseous products into the gas phase. It is also noteworthy that maximum rates of mass transfer are not invariably optimal: the partial disinhibition of

methanogenesis depends on the protective effect of mass-transfer limitations in Zone C. In contrast, none of these steps is likely to be limiting in anaerobic digestion. When acid inhibition can be prevented by controlling the feed rate, the process steps are not physically separated, so no mass transfer steps are involved. Thus, process models based on AD are unlikely to be useful.

This micro-reactor model is consistent with many process observations, some previously obscure. The model suggests that improved acid transport is the reason for the observed benefits of high moisture levels. (An alternative possibility, not considered here, is that free water assists the diffusion or effectiveness of hydrolases, perhaps relieving steric hindrances.) Few seed fragments are in good contact with waste over their whole surface, as assumed in the model. Moreover, real waste is far from the ideal of a homogenous mass. Free moisture might, therefore, maximize the utilization of surface through which acids can escape from Zone B, thus accelerating acetogenesis. Moisture movement would enhance this effect. It is noteworthy, however, that the essential mechanism is the relief of acetogenesis from product inhibition, not the supply of substrate for methanogenesis.

Compression of the waste may be stimulatory for similar reasons. In the absence of moisture movement, any increase in the contact between rich and lean fragments would stimulate mass transfer. However, the concept of a mobile reaction front, progressing *within* the waste fragments, suggests an alternative mechanism. Voids might block its advance, so increased contact due to compression might simply provide more contact points through which the front could progress from one particle to the next.

A more puzzling observation, landfills producing methane at the same time as acidic leachate[34,35], is readily explicable if methanogenesis occurs only or chiefly *within* the waste fragments. Another observation, methanogenesis in the gravel of basal drainage layers[34,35], might be due to a similar effect, created by channelling. While high-flow areas would be flooded with excess acid, any low-flow areas could provide additional sites for methanogenesis.

An important consequence of the proposed model is that methanogenesis cannot be sustained without an adequate buffer zone. This will depend as much on seed fragment size as on the density and viability of the inoculum. Such a zone can only be established in a fragment big enough to accommodate both a methanogenic zone capable of utilizing the acids as fast as they diffuse in and a buffer zone thick enough to limit the rate of inward diffusion. In smaller seed fragments, methanogenesis would become inhibited and the acidity would rise inexorably, until the seed fragments became part of the ensiled zone[53]. (To stress this point, the conventional term 'particle' has therefore been replaced throughout this paper by 'fragment', to emphasize the irregularity and wide size range of both waste and seed material; 'particle' might misleadingly suggest much smaller sizes, especially in a system that includes microbial cells.) Clearly, the larger a seed fragment is, the higher are its chances of sustaining methanogenesis. However, the risk that mass-transfer resistances will become rate-controlling grows too, so there is an optimum size for seed fragments[53]. This cannot yet be quantified but will be influenced by many variables, including seed viability and waste composition.

The minimum viable size for seed fragments might be quite small but it follows from the observations of Veeken and Hamelers[16] that an isolated methanogen surrounded by fresh or ensiled waste can never become active. Their ingenious experimental design housed a stack of perforated trays, alternately containing seed and waste, through which leachate was circulated. They found that the stimulatory effect of irrigation was due to the transport of nutrients to the seed and not the reverse; any microbial cells transported into the waste trays became inhibited by excessive acidity.

These observations give support to the present model, confirming the need for a critical mass of seed material at any point, to relieve methanogenesis from acid-inhibition. Moreover, they suggest that distribution of the inoculum may not contribute at all to the effectiveness of irrigation: the flow velocity in most parts of the waste may be too low for transport of seed particles large enough to thrive.

It follows that the initial seed distribution determines the rate of digestion. If an independent micro-reactor expands from each viable seed-particle, the overall rate is determined by the number of such micro-reactors and the volume of waste each must expand into in order to complete the process. This in turn is determined by the initial number of seed particles and their spacing.

SSD can be seeded in several ways, of which only the first approaches the optimal conditions suggested above.

(a) Engineered digesters commonly use a seed of stabilized waste, many fragments of which might be big enough to be effective. The optimum seed:waste ratio is of the order of 1:1[4,16,27], which is consistent with a need for a considerable lean mass. This gives rapid stabilization.
(b) Seeding of landfills is not standard practice. Seeding with slurries of digested sewage sludge has been tested but without convincing success. Thus, Barlaz *et al.* considered that such seeding was ineffective[55] while Blakey *et al.*, who also used such seeding, concluded that leachate recycle was the more significant variable[35]. Moreover, although 'seeding with methanogens' is cited as a test variable and reported as having 'helped', no unseeded control was run. The benefit is not quantified and is attributed to both the bacterial and moisture content of the sludge. The latter may have been more significant. The individual flocs in 'wet' sludges may be too small for viability, although a minority might thrive in the lean fraction of the waste. However, their effectiveness would be limited by the consequent maldistribution. (Dried sludges could include coherent fragments large enough to be viable but are rarely available in the temperate climates where these trials were done.)
(c) When no seed is added to a landfill, the natural flora can initiate SSD. Although the natural methanogen population is low, this is offset by a tendency towards localization in suitably lean micro-environments, such as soil from garden and construction wastes.

Thus, seeding trials using ineffective sludges may have added little to the performance obtained with the natural inoculum alone. This has led to a widespread belief that landfills will not respond to seeding. This conviction may be mistaken. If the present thesis is correct, effective seeding could lead to greatly accelerated forms of SSD.

The sub-optimal initial conditions in cases (b) and

(c) could explain the apparently bistable behaviour of landfilled waste: areas with adequate seeding proceed relatively quickly to methanogenesis, and eventual stabilization, while areas without it 'fail', to the metastable ensiled state. This might give rise to the large undegraded masses found in old landfills and the marked rate differences between the faster and slower areas of many landfills. More uniform seeding might eliminate such failures.

The proposed model could also explain some apparently inconsistent reports on the effects of size reduction[38,39]. The objective of shredding is usually to improve compaction or to accelerate hydrolysis but the effect on any seed fraction might be more significant. If seed fragment size is more critical than waste size, moderate shredding might disperse the seed and also increase the number of seed fragments by division. However, the pulverization or homogenization commonly practised in laboratory studies might easily reduce the seed fragments to below the minimum effective size.

Although particle size clearly requires more attention in research, it is not easy to measure in wastes. Many laboratory studies quote no size data, while others specify only the maximum size remaining after a size reduction step. The reports that do cite size data include one on recalcitrant wastes, in which the best results were obtained with 0.35 mm particles, the smallest tested[60]. However, such wastes are less dependent on optimal seeding. On municipal solid waste, perhaps more significantly, performance did not improve below an average size of 2.2 mm^3.

Even without excessive size reduction, some failures of laboratory-scale studies[54,55] might be due to inadequate seed fragment size. Seeding with anaerobic sludges is common[57–60], although not universal[61], at small scale. In a landfill, masses of such materials as paper can provide ideal micro-environments for this seed to infiltrate, although the inerts may contribute too. In laboratory work, however, waste samples are commonly hand-sorted to remove large inerts[26,27,62], then the remainder is often finely shredded, or even pulverized[61–67]. Such pretreatments may thus exclude one of the protective fractions, while applying excessive size reduction to the other. Seeding with stabilized waste[27,54,62] avoids the need for a separate lean fraction but this too could be over-shredded.

An alternative experimental approach is to work on composted feedstock, perhaps mixed with fresh waste, or on partly degraded waste extracted from a landfill or digester[55,62,68]. Both reduce the likelihood of excessive acidification and the latter also introduces well-populated seed fragments of effective size[53]. However, the results might simply be inapplicable to the very different conditions in raw wastes, so of use only where pre-composting is envisaged in full-scale operation.

Thus, in a typical landfill accepting raw waste, the rate of stabilization may depend more on the number, distribution and size of seed fragments than on the composition or fragment size of the waste. Seed fragments need only be large enough to ensure that effective fragments are common. Larger fragments would be more certain to develop but, for an equal mass of seed, their wider spacing would introduce avoidable mass-transfer resistances. A large number of well-dispersed, small seed fragments might therefore be better than fewer large ones. This strategy would maximize the number of micro-reactors while minimizing the volume to which each must grow to complete the process of waste stabilization. Pretreatment to achieve this for landfilled wastes might require finer shredding and more mixing than is now usual. This would be costly but the benefits in process acceleration and reliability might be great.

Current landfill practice is far from this optimum seeding strategy but it might be approached in many waste digestion plants. The stabilized waste used as seed at a 1:1 ratio has a wide range of fragment sizes, so that many fragments might lie within the optimum range. (Indeed many may be oversized, thus wasting space.) Such seeding is not currently contemplated in landfills, because of the cost of site volume. Although landfill capacity is commonly costly and scarce, digester capacity is much more expensive, so this difference over seeding might seem irrational. However, a high seeding rate greatly reduces residence time in the digester, raising volumetric efficiency in proportion. As landfill sites are rarely re-used for further disposal after closure, volumetric efficiency in this sense is not currently a major issue in design. It may become so in future, if a modest addition of seed is proved to quickly release more volume than it occupies, by accelerating breakdown of the waste.

The proposed micro-reactor model may not be unique in microbial systems but it is certainly unusual. Requirements for a minimum inoculum size or for its localization are known, often deriving from a need to minimize the dilution of extracellular metabolites. However, the concept of an advancing reaction front, incorporating distinct reaction zones, appears to be novel.

There is, however, an interesting parallel with work on auto-catalytic chemical reaction. Vavilin and Zaikin report a case where reaction time was minimized by commencing the process without mixing, in order to allow a 'critical mass of hot particles' to develop, before mixing to accelerate the reaction[69]. However, this operating regime might not be applicable in SSD, in which mixing is costly and only effective at macro-scale.

MODEL VERIFICATION

New process models based on the micro-reactor model would give effective support for the improved seeding strategies suggested above. However, a full model might need to allow for the heterogeneity of the media, for the gradual transition between inhibited and uninhibited states, for poor contact between waste and seed, for the effects of free water and of moisture movement, for mass transfer of components other than acids, for a true geometry approximating to a set of concentric but irregular spherical shells, for phase inversions (in which the seed surrounds the waste), for the variability of the pre-methanogenic lag phase and for non-ideal distribution of the seed. The development of so complex a model might take some time.

The alternative of direct experimental verification of the physical model might be equally difficult, because of the expected thinness of the reaction zones. In principle, an array of pH microelectrodes could be used to detect the reaction front and measure its thickness and velocity. A comparable study of the termite gut, also a micro-environment for obligate anaerobes, shows that very steep concentration gradients can be measured in natural systems[70]. The potential inhibitor here is oxygen, rather than volatile fatty acids, so the protective reaction is

oxygen utilization by facultative anaerobes. However, the interactions between mass transfer and reaction are comparable and create concentration gradients on a micrometre scale. The chemistry differs but the physical model could be similar. Consequently, the zones making up the reaction front in BSSD might also be only a few micrometres thick and yet amenable to study by similar experimental methods. However, this method is unlikely to give quick results.

Another approach would be to observe process kinetics under well-defined system geometry. As noted above, process acceleration might not depend on microbial growth. However, an expanding sphere grows in area, so the volume of the rate-limiting zone will increase if its thickness is limited only by mass transfer effects. The process could therefore accelerate gradually, with or without growth. This would continue until neighbouring shells begin to overlap, as the ensiled waste between them is consumed. Process deceleration would follow. System geometry would determine the variation of reaction rate with time.

Initial experimental plans are, however, to proceed directly to a demonstration of the scope for process acceleration implied by the model. Lysimeters charged with simulated waste and seed materials of well-defined size will be monitored. This is expected not only to give support to the model but also to point towards immediate operational benefits.

CONCLUSIONS

A micro-reactor model of solid-state digestion is proposed. It is based on the separation of successive reaction steps in adjacent thin zones, linked by potentially rate-limiting mass-transfer processes. The rate-limiting step seems likely to be the relief of acid inhibition of the hydrolysis-acidogenesis-acetogenesis pathway. The mechanism of this is the diffusion of acids into an inactive buffer zone separating the acetogenic zone from the methanogenic zone. These three zones form a reaction front, which gradually advances into the waste from each seed particle of viable size. This reaction front is the site of reaction for readily-degraded organic matter; the more resistant substrates are degraded after it has passed. The essential process is thus asynchronous, heterogeneous and micro-scale. Consequently, attempts to induce SSD to conform to alternative reaction models may be futile or even deleterious.

The model also suggests that seeding techniques might be crucial. Seed fragments well dispersed and big enough to provide sheltered micro-environments for methanogenesis might effect substantial process acceleration. Each develops into a discrete micro-reactor, which slowly expands into the surrounding waste. The rate of stabilization thus depends on the spacing of the seed. Seeding may be far from optimal in most landfills, yet the cost of better seeding is unlikely to be high. The economic benefits of a much faster and more reliable process could be substantial. It could also relieve many of the doubts over landfill as a sustainable method of waste management.

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ADDRESS

Correspondence concerning this paper should be addressed to Dr D. J. Martin, Department of Chemical and Environmental Sciences, University of Limerick, Limerick, Ireland.

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