Microbiology of Landfill Sites

Editor
Eric Senior, Ph.D.
Lecturer in Applied Microbiology
Department of Bioscience and Biotechnology
University of Strathclyde
Glasgow, Scotland

1990

CRC Press, Inc.
Boca Raton, Florida

7174

Received by ER-RPF
SEP 03 1998
TMA

59065

Chapter 5

LANDFILL GAS

Eric Senior and George B. Kasali

TABLE OF CONTENTS

I. Introduction 114

II. Control and Optimization of Methanogenesis 114
- A. Methanogenic Pathways 114
- B. Metabolic Requirements 119
  - 1. Production Constraints 119
- C. Methane Fates 121
- D. Methane Optimization 121
  - 1. Refuse Composition and Pretreatment 122
  - 2. Moisture Content and Refuse Density 123
  - 3. Temperature 130
  - 4. pH and Alkalinity 134
    - a. pH 134
    - b. Alkalinity 140
  - 5. Role of Hydrogen 144
  - 6. Effects of Carbon Dioxide and Methane 146
- E. Site Strategies 148
- F. Alternative Gas Generation Strategies 148
- G. Gas Abstraction, Treatment, and Uses 150
  - 1. Abstraction 150
  - 2. Treatment and Storage 151
  - 3. Gas Uses 152

References 152

I. INTRODUCTION

Traditionally, landfill gas, which may be constituted by more than 80 different components (Table 1),[1-4,195] has attracted little attention, although as the composition, particularly the methane content, has changed with time, due essentially to changes in refuse composition and site practices, it has increasingly been regarded both as a liability as well as an energy recovery opportunity.[5-7] Particular problems of uncontrolled gas release, by convective flow due to pressure gradients[5,8] and by molecular diffusion due to low gas concentration regions, include odors,[4,9-11] explosions and fires, groundwater acidification,[12] and reduced crop yields, including complete diebacks,[13] due to a combination of factors such as sensitivities to carbon dioxide, methane, oxygen limitation, elevated temperature,[7] hydrogen sulfide, ethylene, and mercaptans.[13] In an attempt to minimize these problems, control of lateral gas migration from shallow sites, which may be monitored by aerial thermophotography,[14] to comply with discharge limits such as 5% (v/v) at the site boundary,[15] may be effected by use of gravel-filled cut-off barriers or trenches. For deeper sites (>6 m), however, gas abstraction systems or air injection systems have been shown to be more cost effective.[7] As an alternative, gas seals of natural materials or fabricated membranes may be employed, although these represent considerable unrecoverable expense.[16] Conversely, vertical gas migrations may be controlled comparatively cheaply by use of low pore-size soils, particularly clay soils,[7] although these do present potential problems for gas monitoring.[17]

Once controlled, the possible environmental impacts of the gas may be negated by either flaring[18] or soil sieving.[19] Soil sieving, which tends to be more effective in winter,[20] involves the use of low pore-size soils, first to trap and then to oxidize, by aerobic intervention, the reduced malodorants.[9,19]

Although still largely untapped, the methane content of landfill gas, which was recognized as long ago as 1934 by Jones and Owen,[21] does represent a reservoir of tremendous potential since it has been estimated that annual productions in the U.S. and U.K. now exceed 200 billion ft^3 and 2000 million therms, respectively.[21] The attractiveness of using this gas as a source of energy can be readily assessed by consideration of the increasing volumes of natural gas recovered by man which in 1965 accounted for 520 million m^3, although by 1979 this total had more than tripled.[22] Until recently, biogas has often been regarded as an asset, without detailed consideration of the costs entailed in realizing the energy potential of 24 MJ/m3,[23] although until used or sold, it is a waste product and, as such, represents a liability.

II. CONTROL AND OPTIMIZATION OF METHANOGENESIS

A comprehensive understanding of the microbial ecology of methanogenesis within the refuse mass is fundamental to either control or optimize gas production.

A. METHANOGENIC PATHWAYS

In view of the diversity of methanogenic precursors (Chapter 2) it is perhaps pertinent to identify the pathway(s) operative within the refuse mass. In anoxic environments, other than landfill, it has been estimated that 70% of all methane generated is derived from acetate,[24-26] with the remainder from H_2/CO_2, and, to a lesser extent, formic acid, H_2/CO, propanol, methanol, and methylated amines.[27] In the presence of high concentrations of sulfate, however, methanol and methylated amines have been shown to replace acetate as the major methanogenic precursors.[28-30] Also, two mechanisms of methanogenesis from methanol have been described, depending on the presence or absence of acetate as a cosubstrate.[31] A simple radiotracer study[32] with refuse cores showed that of the three substrates — acetate, bicarbonate, and methanol — the highest rates of methanogenesis were recorded with methanol (Table 2). However, since the pool size of methanol in the refuse was below the limits of detection, then not only could the

TABLE 1
Constituents of Landfill Gas[1-4,195]

	Concentration range	
	Volume %	ppm
Acetone		32.5
Argon	0.01—0.05	
Benzene	0.08—0.11	5.5
C_1-substituted benzenes		9.8
C_4-substituted benzenes		7.6
Butyl benzene		0.063—0.138
Butyl benzenes		0.032
Dichloro benzene		4.1
Dichloro benzenes		0.016
Ethyl benzenes		21.4
Pentyl benzenes		0.018
Propyl benzenes		0.069—0.120
n-Butane	0.006	184
iso-Butane	0.004	122
Butane thiol		
1-Butene		18
Butyl alcohol		5.2
Butan-1-ol		>0.019
iso-Butan-1-ol		>0.005
Butan-2-ol		>0.022—0.210
Butan-2-one		0.020—0.026
Carbon dioxide	30—40	
Carbon tetrachloride		0.011
Chloroform		0.61
Decanes		0.081—0.252
n-Decane		0.045—0.140
Decenes		0.013—0.092
1,2-Dichloroethane		[illegible]
t-1,2-Dichloroethene		59
Dichlorodifluoromethane		0.023
Diethylether		0.020
Disulfides	0.93—1.65	
Dimethyl sulfide		0.004—0.040
Ethane		22
Ethanol		0.650
Ethyl acetate		0.008—0.064
Ethyl butanoate		0.004—0.015
2-Ethyl-1-hexanol		[illegible]
Ethyl mercaptan		[illegible]
Ethyl pentanoate		[illegible]
Ethylene		20
Heptane	0.292—0.450	
Heptanes		0.004—0.007
n-Hexane	0.128	0.013
Hexanes		0.014
Hexenes		0.0026
C_4—C_{14} hydrocarbons		114.2
Hydrogen sulfide	0.0017—0.91	
Limonene		26.2
Mercaptan sulfur	0—0.33	
Methane	40—50	
Methane thiol		0.087
Methanol		0.210
Methyl ethyl ketone		5.2

TABLE 1 (continued)
Constituents of Landfill Gas[1-4,195]

	Concentration range	
	Volume %	ppm
2-Methyl-fluran		6.9
Methyl pentanoate		0.022
Methyl styrene		0.015
Nitrogen		
Nonanes		0.031—0.100
n-Nonanes	0.064	0.019—0.083
Nonenes		0.012—0.021
n-Octane	0.206	0.006—0.012
Octanes		0.009—0.015
Octenes		0.004
Oxygen	1	
n-Pentane	0.014	196
iso-Pentane	0.01	83
Pentanes		0.040
Pentan-2-one		0.004
Perchloroethylene		19
Propane	0.007	141
Propan-1-ol		0.073
Propan-2-ol		0.017—0.046
Propyl cyclohexanes		0.004—0.005
Sulfides	0.041—1.80	
Terpene		12.4
Terpenes		0.033
α-Terpinene		11.1
Tetrachloroethylene		0.003—0.030
Toluene	0.05—0.09	150
1,1,1-Trichloroethane		0.018
Trichloroethene		13
Trichloroethylene		0.011
n-Undecane		0.021—0.051
Undecanes		0.048—0.164
Undecenes		0.034—0.054
Vinyl chloride		44
Xylene		14.9
Xylenes		0.036—0.077

absolute rates not be determined, but also the relative rates must be questioned. In a similar study by Kasali[33] the methanol and acetate pathways were again shown to be dominant, although in this case the rates of conversion were found to be comparable. Unlike the first study, however, an operative $NaH^{14}CO_3$ pathway was also detected.

Although neither of these studies resolved the question of the relative contributions of the different methanogenic pathways, Hoeks and Borst[34] exemplified the role of acetic acid in landfill gas generation when they reported that methanogenesis was accompanied by a decrease in leachate acid concentration. Subsequently, inhibition of methanogenesis was shown to result in an increase in the concentrations of short-chain fatty acids in the leachate. These results were perhaps not surprising since it has been reported that during the anaerobic dissimilation of organic compounds, in ecosystems other than landfill, the production and utilization of acetate are quantitatively the most important metabolic steps.[35] Under anoxic conditions, acetate can be produced, by the intervention of single species and interacting microbial associations, from a

TABLE 2
Methane Generation Rates from Labeled Precursors

% Conversion of [^{14}C] Label/g Wet Weight/d		
[u-^{14}C] Acetate	$NaH^{14}CO_3$	[^{14}C]Methanol
0.09	BD	24.55
0.03	BD	2.35
0.41	BD	44.58

Note: BD denotes below detection.

Senior, E. and Balba, M. T. M., unpublished observations

variety of substrates including carbohydrates,[36] aromatic monomers,[37] volatile fatty acids,[38] alcohols,[39] and H_2/CO_2.[40-42] The formation of acetate from many of these substrates by fermentative bacteria, however, usually requires the presence of hydrogen sink organisms, such as sulfate-reducing bacteria and methanogens, to maintain, overall, a negative free energy change.

Examination of the role of this key intermediate in the overall mineralization of the refuse was made by Coutts[43] with a hexanoic acid-dissimilating microbial association isolated from landfill.[44] In the presence of sulfate, hydrogen, the β-oxidation product of hexanoate and butyrate, was competitively utilized by the component sulfate-reducing bacteria, whereas in the absence of sulfate, an interaction between hydrogen-utilizing acetogenic and methanogenic bacteria facilitated hydrogen removal, with acetate catabolism restricted to the methanogenic bacteria (Figure 1). Since, as speculated by Rees,[45] methanogenesis from H_2/CO_2 is probably limited by hydrogen availability in landfills, the dominant pathway would appear to be aceticlastic methanogenesis.

In view of the dominance of acetate as the major methanogenic precursor in anoxic environments, it is perhaps surprising that metabolism of this molecule has been detected in only two genera, *Methanosarcina* and *Methanothrix*.[39,49,50]

By use of the methanogenic inhibitor 2-bromoethanesulfonic acid, Kasali[33] demonstrated that an operative methanol methanogenic pathway was present in fermenting refuse, thus confirming the potential indicated in his radiotracer studies. Although the actual species involved were not identified, it has been shown[28] that *Methanosarcina barkeri* and *Methanococcus mazei* both effect this conversion. In landfill, the most likely sources of methanol are lignin and the hemicellulose, pectin. Although different types of pectin may be recognized, essentially the molecule consists of rhamnose and unbranched chains of α-(1-4) glycosidically linked D-galacturonic acid units which are either partly or completely esterified with methanol. In the absence of oxygen, species such as *Clostridium butyricum* demethoxylate the polymer by use of pectin esterases which split the methyl-ester bonds to liberate methanol.[51] In landfill the potential exists that the sulfate-reducing bacteria and methanogens compete for methanol. Kasali,[33] however, showed that in radiolabeled refuse core samples, methanol was completely converted to methane, thus agreeing with earlier reports for anoxic salt marsh sediments.[52]

In addition to the three methanogenic substrates — acetate, bicarbonate and methanol — methylated amines have also been examined.[53] Methylated amines, which may be generated either from the dissimilation of molecules such as choline, creatine, and betaine, or by bacterial reduction of trimethylamine oxide,[52] have been shown to be significant sources of methane in a variety of anoxic ecosystems.[30,53] Although the methyl groups of trimethylamine and monomethylamine have been shown[54] to be reduced to methane by species such a *Methanosarcina barkeri*, Kasali[33] was unable to detect a monomethylamine pathway in refuse core

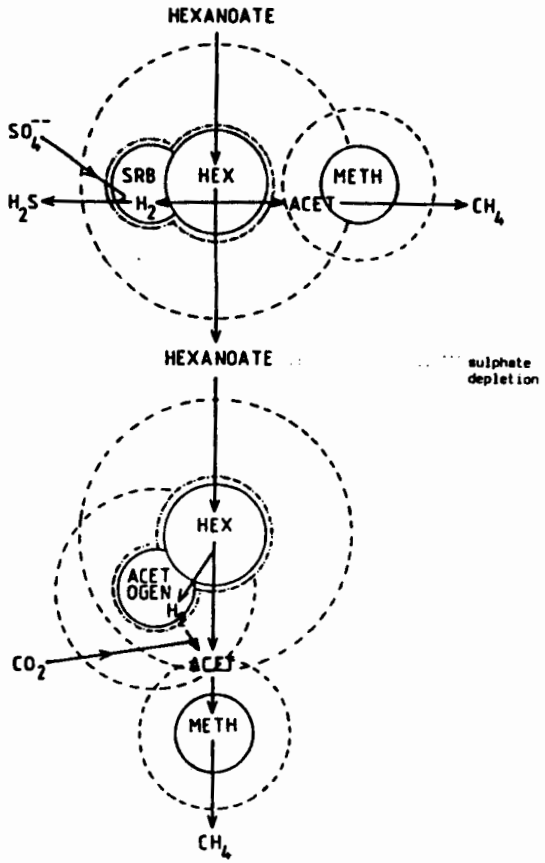

FIGURE 1. Scheme for anoxic hexanoate catabolism by an interacting association, isolated from landfill,[43] in which the hexanoate-catabolizing species and sulfate-reducing bacteria or hydrogen-utilizing acetogens formed obligate first-tier associations in the presence and absence of sulfate, respectively. These species together with the methanogenic bacteria then constituted a second-tier association. The solid lines represent habitat domains, and the broken lines activity domains. Hydrogen utilization was closely associated with the habitat domains of the first-tier associations, whereas acetate catabolism was more prominent in the second-tier interactions.[43] (From Coutts, D. A. P., Senior, E., and Balba, M. T. M., *J. Appl. Bacteriol.*, 62, 251, 1987.)

samples. Conversely, a trimethylamine pathway was detected, and this, together with the fact that the molecule has been found to be present in landfill leachate,[55] suggests that this pathway is operative in landfill. In this situation the most likely source of trimethylamine is betaine, which is a constituent of plant and animal tissues.

Although there has been a paucity of studies on refuse catabolism, it may be speculated that it is only a matter of time before most, if not all, of the methanogenic pathways are confirmed in landfill.

B. METABOLIC REQUIREMENTS

Despite the great diversity of morphology, of the increasing number of both genera and species of methanogenic bacteria, together with physiological and kinetic differences, these bacteria do share unifying physiological and biochemical features[25,26,46,56–60] such as their high substrate specificities and their unusual array of cofactors including coenzyme M,[61] F_{420},[62] F_{430}, and F_{342}.[63] Other unique properties include the requirement for a low redox potential (<–150 mV and, in some instances <–330 mV) the presence of coenzymes 7-methylpterin, methanopterin (2-amino-4-hydroxpterine),[64] methyl-tetrahydromethanopterin, and methanofuran; the distantly related 16S rRNA compared with other prokaryotes; the differences in the common arm of the tRNA; the absence of both D-amino acids and muramic acid in their cell wall; the lipid components of phytanyl ether glycerols and squalenes; the low genome size; the absence of quinones and the presence of cytochromes in only a limited number of cases; the possession of a novel CO_2 fixation pathway;[65–67] and the presence of a possible phosphorus reserve material.[68]

In addition, these species have common growth requirements for inorganic sulfur,[61,69–73] with 3 mg/l sulfide and 0.88 m*M* total sulfur required for methanogenesis from CO_2/H_2 and cellulose, respectively;[74] ammonia,[57] which may be facilitated by formation of microbial associations with amino acid-degrading bacteria;[75] and trace elements such as iron, cobalt, and, more particularly, nickel which is an essential component of the coenzyme F_{430}. Although all of these requirements are either present at refuse emplacement or are generated during subsequent catabolism, it is possible that, with time, they may become limited.

Methanogenesis, with one exception,[59] requires a near neutral pH and although this, according to Robinson and Maris,[76] could be facilitated by the presence of ammonia, it has been suggested[77] that there is a temporal separation of fatty acid and ammonium productions in landfill. This inference was, however, drawn from data of relative concentrations of fatty acids and ammonium and not from a definitive experiment. Nagase and Matsuo[75] have, in fact, presented good evidence to show that in anaerobic digesters microbial associations exist of amino acid-degrading bacteria and methanogens. Thus, it may be speculated that similar interacting associations could be present in landfill.

1. Production Constraints

Despite the availability of essential requirements, the landfill ecosystem does represent an extremely competitive and hostile environment to the methanogens (Figure 2).[78] Farquhar and Rovers[12] defined three groups of interacting factors (A, B, and C) which affect gas production in landfill. Group A factors (temperature, aeration, moisture content, E_h, pH, alkalinity, nutrition, and toxic compounds) were regarded as features of the immediate microbial environment of the methanogens, within which gas generation occurs. These variables are not, however, static, but change in response to both the Group B factor of infiltration and the Group C factors of air temperature, atmospheric pressure, placement and cover, precipitation, topography, hydrogeology, and refuse composition. Of all these variables, Farquhar and Rovers[12] speculated that some control may be exerted during landfill design and operation on refuse composition, hydrogeology, topography, placement, and cover. As a result of developments in refuse handling and landfill practices, however, consideration should also be given to factors such as pretreatment, emplaced density, and exposure to air.

Within the refuse mass, interspecies competition is a major determinant since competition with reductive-deaminating, nitrate-reducing, and sulfate-reducing bacteria for common precursors, particularly electron donors, may be regarded as the major constraint of methane production. Thus, in the presence of exogenous electron acceptors such as nitrate and sulfate, sequential utilization ($NO_3^- > SO_4^{2-} > HCO_3^-$) is apparent, the actual order of which may be predicted on thermodynamic grounds according to the increment of energy liberated from a common electron donor as it is oxidized by each of the acceptors.[79] Predictions such as these

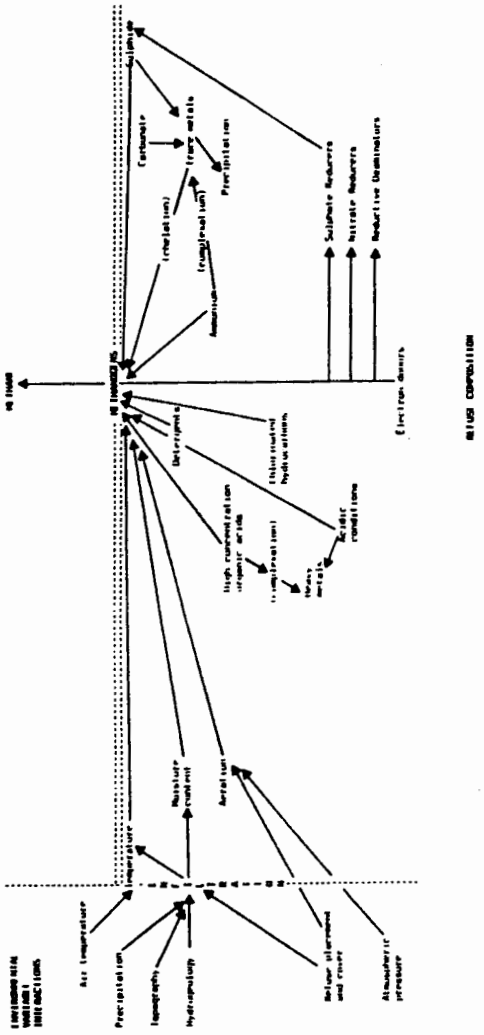

FIGURE 2. Methanogenesis production constraints in the landfill ecosystem.

must be made with a degree of caution, however, since other factors, including kinetic considerations, substrate uptake, and subsequent transport, all play key integral roles.

In addition to exogenous inorganic electron acceptors, many other chemicals may be present in refuse to challenge, either directly or indirectly, methanogenic bacteria.[12,80,81] For example, chemicals such as chlorinated hydrocarbons and detergents are directly toxic, as, too, are heavy metals, although here the presence or absence of chelating or precipitating anions and the pH regime must be considered. Despite the potential toxicity of heavy metals, it has been reported by Ehrig[82] that their presence in solid waste does not influence the sensitive methanogens to a high degree.

Together with these constituents, products of refuse catabolism can also exert direct and indirect inhibitory effects. For example, an extremely low partial pressure of the fermentation product hydrogen must be maintained, by interaction of proton-reducing bacteria with obligate hydrogen sink bacteria,[83-84] to facilitate favorable thermodynamic conditions and, so, prevent accumulation of reduced organic acids such as propionic, lactic, butyric, valeric, and caproic which could prove inhibitory, either as a concentration and/or pH effect, to subsequent catabolic processes, particularly methanogenesis. If the hydrogen sink is provided by sulfate reduction, then the production of un-ionized hydrogen sulfide poses a direct toxic threat to methanogens at concentrations in excess of 50 mg/l,[23] although even the presence of nontoxic concentrations may inhibit methanogenesis by precipitating essential trace elements. In the absence of sulfate, however, sulfate-reducing bacteria may act as syntrophic acetogens, on intermediates such as lactic acid or ethanol, by switching from sulfate reduction to hydrogen formation by proton reduction.[85-87] Finally, although methanogens have an obligate requirement for ammonia, the concentration must be maintained below the minimum inhibitory value of 0.4 g/l.[23]

C. METHANE FATES

Once formed, methane, which if not removed, may effect product inhibition,[88] potentially may be reoxidized to carbon dioxide by sulfate-reducing bacteria,[89] methanogens,[58] or aerobic methanotrophs[17] prior to recovery (Figure 3).

D. METHANE OPTIMIZATION

According to Stearns and Wright[3] methane has a theoretical maximum production of 0.266 m^3/kg refuse, although volumes as high as 0.450 m^3/kg wet refuse as received have been calculated by other workers.[90] Estimates like these are usually determined by use of an equation such as the following:[90]

$$CaHbOcNdSe + \left(a - \frac{b}{4} - \frac{c}{2} + \frac{3d}{4} - \frac{e}{2}\right)H_2O \rightarrow \left(\frac{a}{2} + \frac{b}{8} - \frac{c}{4} - \frac{3d}{8} - \frac{e}{4}\right)CH_4$$

$$+ \left(\frac{a}{2} - \frac{b}{8} + \frac{c}{4} + \frac{3d}{8} + \frac{e}{4}\right)CO_2 + dNH_3 + eH_2S$$

or other kinetic models.[5] Thus, theoretically, the mineralization of paper should result in 51% CH_4 and 49% CO_2 while the dissimilation of fat should give 71% CH_4 and 29% CO_2. By using an equation such as this, then theoretical predictions of potential gas volumes may be made with respect to changes in refuse composition. However, as discussed by Ham,[90] calculations of this type are based on a number of assumptions which are not valid in the refuse mass. Specifically, assumptions are made so that (1) complete mineralization of all refuse components results, (2) two products only, methane and carbon dioxide, are formed, (3) a balance of substrates and nutrients is available at all times, (4) and no portion of the dissimilated refuse components is utilized for cell synthesis. As a consequence, Ham[90] suggested that a more realistic estimate for recoverable methane was 0.047 m^3/kg, with the discrepancy accounted for by a combination of

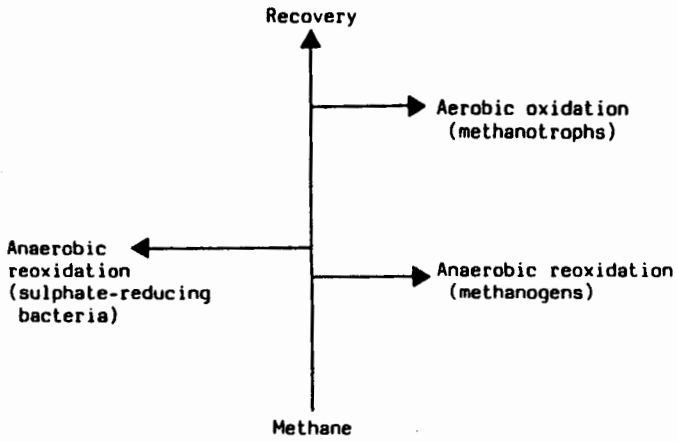

FIGURE 3. Methane fates in the landfill ecosystem.

factors such as the production constraints and gas fates, discussed above, losses between withdrawal wells or near site boundaries, and gas generation at times other than during active refuse fermentation when gas recovery was unlikely. Ham[90] comprehensively reviewed gas production rates from municipal refuse by examining 38 reports in which laboratory studies, lysimeters, pilot-scale landfills, and test landfills were used to examine gas generation from untreated refuse and digested refuse (with and without sewage sludge supplementation). Ranges of estimated, measured, and theoretical rates were reported as 3.7 to 190, 0.21 to 400, and 16 to 450 l/kg/year, respectively, from which Ham[90] concluded that during the more active period of methane production, a reasonable rate of generation would be between 3.1 and 37 l/kg/year.

Attempted optimization of methanogenesis by manipulation of a specific site variable necessitates a prior understanding of its function relative to the ecosystem as a whole. Thus, the task of delineating the more important variables is complicated by the interactions between them. According to White and Plaskett[91] the optimum conditions for methanogenesis in landfill are the following: a temperature range of 29 to 37°C; an absence of air; a pH range of 6.8 to 7.2; a moisture content in excess of 40%; and an absence of toxins. However, from the findings of Boyle,[92] these ideal conditions are rarely found in landfill sites. Boyle[92] reviewed the results of both laboratory studies and pilot-scale operations at the Palos Verdes, Sheldon-Arleta, and Mountain View, U.S. landfill sites and concluded that the landfill did not serve as an efficient bioreactor for the following reasons: the moisture content was low; temperature variations were wide, and normally suboptimal; stratification of compacted refuse was common, thus resulting in pockets of biological activity; contact between the microorganisms and labile refuse components was inefficient; and gas production was unpredictable, due to landfill practices, site characteristics, and cover.

Since, in many instances, any attempts to optimize methanogenesis within the refuse mass must not interfere with the day-to-day operation of the landfill, the number of potential variables for manipulation is limited to refuse composition and pretreatment, exclusion of toxic or inhibitory materials, nutrient addition, permeability and porosity, refuse density and moisture content, temperature, pH and alkalinity, and microbial seeding.[5]

1. Refuse Composition and Pretreatment

Refuse composition, as discussed by Ham,[90] is a major determinant of both gas quality and

rate of production.[93] Thus, although the concentration of generated methane is characteristically within the range 50 to 70% (v/v), variations may be mediated by the degradation of specific refuse components.[90] Similarly, the rates of gas generation will change in response to the lability of these components.

Pretreatment strategies, motivated by economic factors, may similarly effect dramatic changes. Milling, shredding, or pulverizing refuse all facilitate significant volume reduction and confer homogeneity to the rather heterogeneous crude refuse. At the same time the absorptive capacity of the refuse may be increased by a factor as high as three.[94] The net result is, thus, a significant increase in the decomposition rate of the refuse within the landfill. de Walle et al.,[1] for example, demonstrated that particle size reductions from 250 to 25 mm increased the gas production rate from 0.73 m^3/t/year to 4.75 m^3/t/year. Unfortunately, the major component of this gas was carbon dioxide, and methanogenesis was only detected in pH-buffered unpulverized refuse. Increased gas production rates in homogenized refuse may be attributed to a combination of increased surface area, for extracellular enzymatic attack,[45,95,96] and introduction of oxygen, resulting in a shift in fermentation balance toward carbon dioxide. Methane production rates of 60 m^3/t dry solids per year have, however, been obtained with pulverized refuse,[97] although here the fermentation was made with pH control and a high solids concentration (42% w/w), with an inoculum of methanogenic bacteria.

2. Moisture Content and Refuse Density

Since according to Verstraete et al.[98] and Buivid et al.[5] the effects of moisture content and compaction are interdependent, any division of these two parameters would seem to be purely arbitrary.

One hypothesis, which is commonly held, is that stabilization of refuse within a landfill may be accelerated by the controlled application of moisture.[99] This is perhaps not surprising since, clearly, the control of water infiltration is central to the modification of all other interacting parameters which directly affect microbial activity. The overall moisture content of a landfill is a function of the refuse moisture content at emplacement, the infiltrated moisture, and the moisture generated by microbial catabolic activity. Moisture as an end product of microbial activity is, however, considered a minor source compared with infiltration.[99] In landfill, moisture determines the mixing, dilution, and flushing of the various refuse components. Thus, the presence of a high water content should enhance the general availability of nutrients and also stimulate bacterial growth directly.[100]

For aerobic species, Dobson[101] demonstrated that a refuse moisture content of 60% resulted in an elevated oxygen uptake rate compared with 40 and 80% poised samples. In a more comprehensive study by Merz and Stone,[102] a steel tank (45.5 m^3) was filled with approximately 14 tonnes of refuse, prior to moisture content adjustment to 41% (w/w), equivalent to an inplace refuse density of approximately 374 kg/m^3. The tank was then sealed and buried with the temperature at ambient (26.7 ± 6.7°C). Although the initial gas production rate was 0.026 l/kg/d, after 60 d the rate had fallen to zero. At this point, the gross moisture content was increased to 48% (w/w) with the result that gas generation recommenced and continued at an average rate of 0.014 l/kg/d for the next 3000 d. Unfortunately, no qualitative gas composition data were reported with this study.

Later, Rovers and Farquhar[103] made a similar, but more realistic, study in which three cells (C1 to C3) were filled with 2428, 2908, and 670 kg of refuse, respectively. Cells 1 and 2 were maintained, unsealed, under field conditions and, as a consequence, were exposed to moisture inputs from rain and from melting ice and snow. Conversely, the third cell (C3) was insulated, maintained indoors, and supplied with artificial precipitation (75% distilled water, 25% tap water). Cell C1 produced methane at a concentration of 17% (v/v), although this was reduced to 6% by the high infiltration conditions of the spring thaw. Conversely, Cell C2 produced no methane, while cell C3, perhaps surprisingly, produced only 2% (v/v) methane. From these

results the workers concluded that rapid infiltration could impede methane production in landfills.

This distinction between moisture volume and infiltration rate was subsequently endorsed by Klink and Ham,[104] who demonstrated methanogenic rate increases of between 25 and 50% in the presence of moisture movement and found that the relationship held even when the total moisture content was constant. From the results of this study it was concluded that moisture content and movement were separate variables affecting landfill methanogenesis. Leckie et al.[98] similarly determined that continuous water infiltration of the refuse mass resulted in higher rates of methanogenesis compared with single-addition controls, although further increases were recorded in the presence of leachate recirculation. This later finding was, thus, in agreement with the results of Klink and Ham,[104] who attributed the methanogenic rate increase to uniform distribution of basic nutrients, methanogenic precursors, and pH.

Despite the number of studies made, the question of the percentage moisture content required to facilitate optimum gas production rate and maximum methane content is still subject to debate. de Walle et al.,[1] for example, determined in laboratory studies that water-saturated refuse (99%, as dry weight) resulted in maximum rates, as did Klink and Ham.[104] Similarly, Rees[105] incubated refuse core samples under anoxic conditions at *in situ* temperature and showed that the highest rate (300 ml/kg dry weight per day) was apparent in material sampled from below the site water table. In addition, these samples were characterized by elevated amylase and protease activities.[106] Rees[105] also examined data from four reports and concluded that landfill gas production was directly proportional to the percentage water content, although he had speculated earlier[77] that it was the logarithm of the rate of gas production which was directly proportional to the percentage water content.

Conversely, Farquhar and Rovers[12] demonstrated maximum gas production at moisture contents between 60 and 80% wet weight. Similarly, de Walle et al.[1] recorded maximum methane concentrations in the presence of a refuse moisture content of 78% and recommended that landfills which were to be used for gas production should be maintained at a moisture content in excess of 75%, but below 100%. This moisture regime was, however, somewhat higher than the 55% reported by Rees[45] to be a contributory factor to the success of the Aveley (U.K.) landfill site as a methane generator.

Kasali[33] used laboratory refuse columns, fitted with graduated gas collection vessels, at ambient temperature (20.5 to 28.5°C) to examine the effects of six moisture regimes (55, 60, 65, 70, 75, and 80% w/w) on gas evolution. After 95 d of incubation, the total volume of gas recovered from the samples was highest with the 75% moisture content, while the lowest was recorded with the 55% sample (Figure 4). Similar results were also observed for methane production alone (Figure 5). These results were, thus, in agreement with the data of Buivid et al.[95] which showed that methane production increased as the moisture content of the refuse was increased to field capacity.

From Kasali's results[33] it was apparent that as the moisture content was raised above 60%, the resultant increase in methane production started to decline, thus suggesting that this discrete moisture regime satisfied the physiological requirements of the methanogens. Since, as noted by Buivid et al.,[95] moisture promotes the mass transfer or the distribution of other methanogenic-enhancement precursors, it may be speculated that once such distributions were optimized, then elevated moisture contents, approaching field capacity, would be of little value since both gas and methane evolution rates would be independent of the moisture regime.

In addition to these interdependencies, it is possible that large water additions may also introduce oxygen, thus delaying initiation of methanogenesis, and may also stimulate acidogenesis (Figures 6 and 7) to the detriment of the initially low and slow-growing methanogenic population.[45] These two possibilities offer a partial explanation for the lower volume of methane generated at the 80% moisture level than at the 60% (Figure 5). Similar results were reported

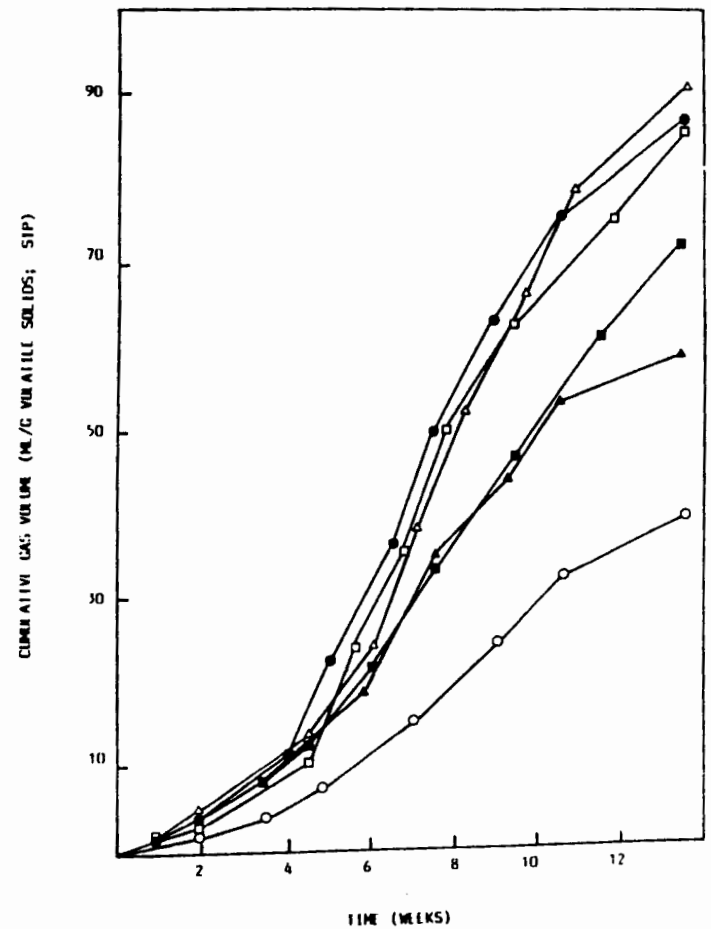

FIGURE 4. Cumulative volumes of gas evolved from ambient temperature (20.5 to 28.5°C, mean 24.3°C) laboratory landfill models[33] in which refuse poised at discrete moisture contents of 55 (○), 60 (●), 65 (□), 70 (■), 75 (△), and 80% (▲) (w/w).

by Buivid et al.[95] who also found a substantial decrease in methane production when the moisture content of municipal solid waste was increased above field capacity to 80%.

Although it is difficult to extrapolate laboratory results to actual sites, which are often characterized by leachate migration, it may be speculated that total waterlogging, particularly during the initial stages of refuse emplacement, could be inhibitory, so that flooded sites or fills extending below the water table may not provide optimum conditions for methane generation.

Together with these studies of the gross effects of moisture on the refuse methanogenic fermentation, Marriott[107] optimized the fermentation moisture indices between 55 and 60% (w/w). Calculation of activation energies in laboratory studies[1] have indicated, however, that the overall reaction rate is chemically controlled and, as such, is not subject to diffusional mass transfer limitations in the presence of high moisture contents.

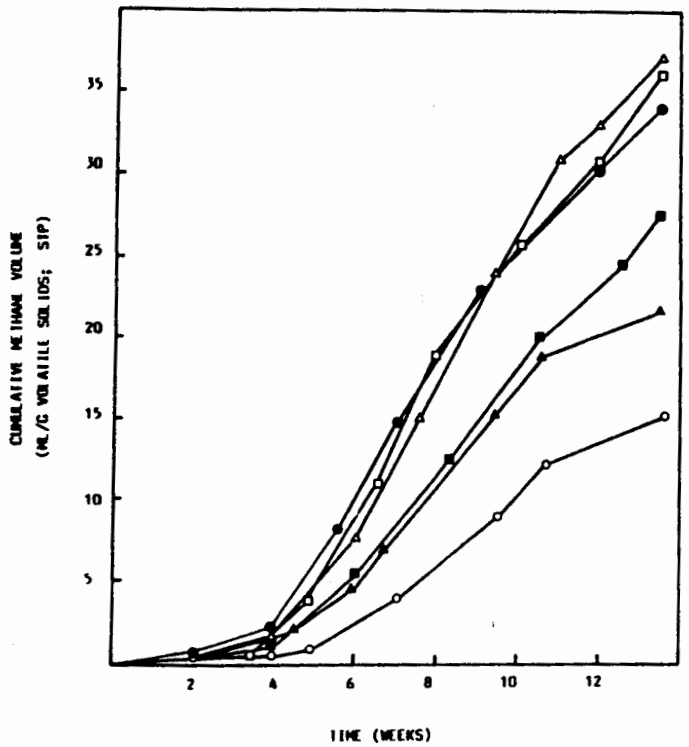

FIGURE 5. Cumulative volumes of methane evolved from ambient temperature (20.5 to 28.5°C, mean 24.3°C) laboratory landfill models[33] in which refuse poised at discrete moisture contents of 55 (○), 60 (●), 65 (□), 70 (■), 75 (Δ), and 80% (▲) (w/w).

In addition to the gas production rate changes discussed above, moisture additions can also mediate significant changes in the refuse fermentation balance. In the presence of low moisture regimes, the solid-state fermentation of refuse has been shown to result in the formation of carboxylic acids and gases,[108] including hydrogen,[106,109] Here, the moisture content of the refuse can either directly affect the growth of the acidogenic bacteria, and thus regulate the production of acids, or, by diluting the acids formed, facilitate pH and acid concentration changes within the microenvironment and, thus, indirectly, affect microbial growth.

Kasali[33] used pulverized refuse in sealed flasks, maintained at ambient temperature (22 to 27°C), to examine the effects of six discrete moisture contents (55, 60, 65, 70, 75, and 80% w/w) on the fermentation balance. After 7 d of incubation, a clear pattern had emerged with increased moisture contents mirrored by increased "total" organic acid (acetate, propionate, and butyrate) concentrations (Figure 7). This picture was also repeated for each of the three individual organic acids. These results were thus in agreement with those of Ghosh,[110] who reported that considerable improvements in a refuse acidogenic fermentation were apparent when the moisture content was increased from 40 to ≤ 60%. As the fermentations continued, however, the pattern became less clear. In addition, a stepwise sequential mode was apparent. From stoichiometric considerations, this mode could not be accounted for by changing rates of methanogenesis and was more likely due to either cessation or retardation of acidogenesis due,

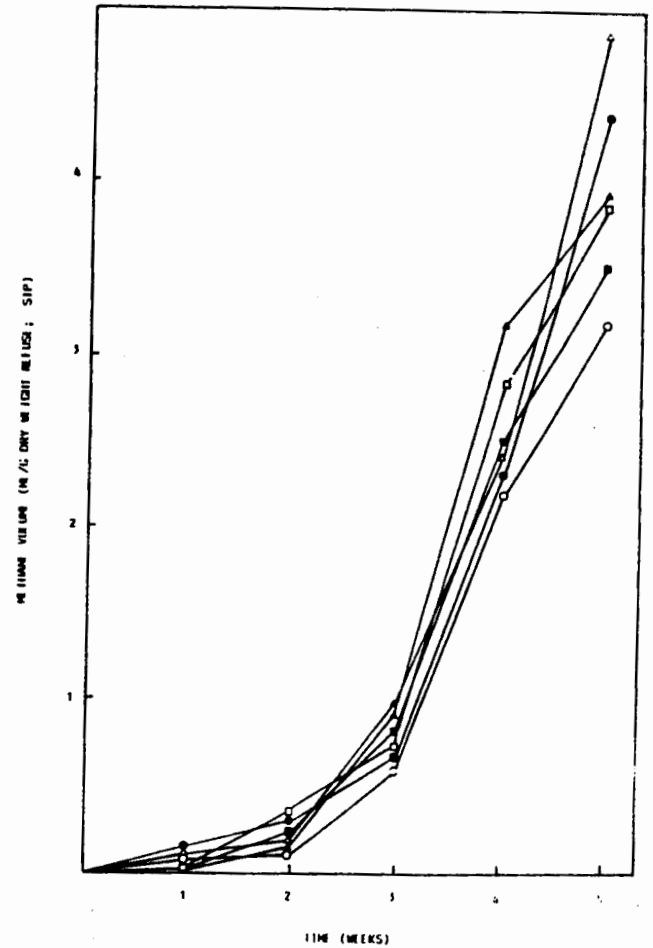

FIGURE 6. Changes in volumes of methane evolved at ambient temperature [illegible] mean 24.2°C) from refuse samples poised at discrete moisture contents of [illegible] 65 (□), 70 (■), 75 (Δ), and 80% (▲) (w/w).

possibly, in part to product inhibition.[111,112] Ghosh[110] also recorded a stepwise sequential acidogenic refuse fermentation and attributed it to the preferential metabolism of a particular organic fraction with sequential induction and synthesis of adaptive enzymes. In the study of Kasali,[33] however, the stepwise sequence of acidogenesis appeared to be a function of the moisture content and not the refuse per se since the phenomenon was not recorded in the 55% poised samples.

It is interesting to note that maximum concentrations of the individual acids — acetate, propionate, and butyrate — were recorded at different moisture contents of 75% (3 weeks), 80% (1 week), and 60% (4 weeks), respectively. Examination of the individual acids, however, showed that consideration of these maxima alone oversimplified a somewhat complicated

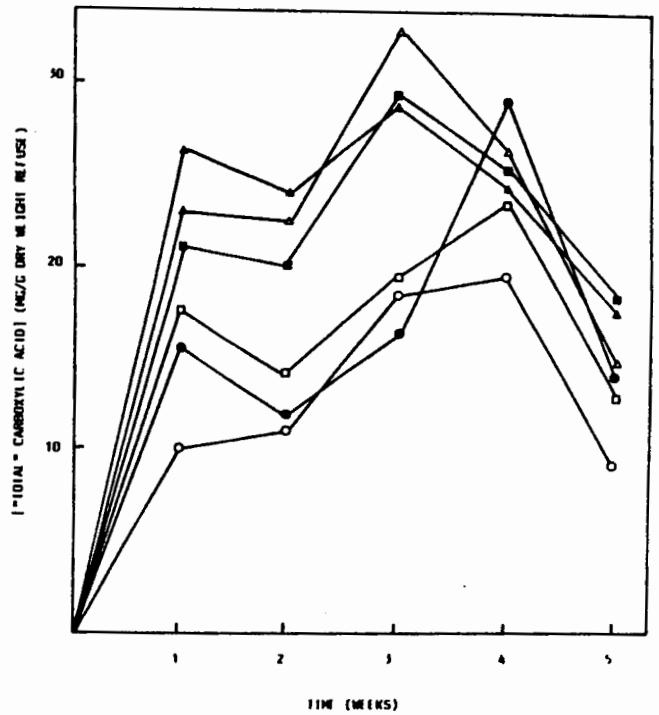

FIGURE 7. Changes in concentrations of "total" organic acids (acetate, propionate, butyrate) at ambient temperature (22 to 27°C, mean 24.2°C) in refuse samples poised at discrete moisture contents of 55 (○), 60 (●), 65 (□), 70 (■), 75 (Δ), and 80% (▲) (w/w).

picture. Thus, although maximum acetate concentrations were recorded in the refuse after 3 weeks of incubation for the 70, 75 and 80%-samples, maxima for the 55, 60, and 65% moisture levels were not recorded until the fourth week (Figure 8). Similar patterns were not, however, apparent for either propionate or butyrate.

Despite possible complication by the intermittent appearance of *iso*butyrate, *iso*valerate, valerate, and caproate, in general, the pH profiles mirrored the "total" organic acid (acetate, propionate, butyrate) profile.

During the course of the experiment, the trends in methane generation from the different moisture-poised refuse samples did not appear to follow any predictable or systematic pattern (Figure 6), although after 3 weeks of incubation, methane production had increased with increased moisture content up to the field capacity of 75%.

In the presence of elevated moisture contents the ratio between methane and carbon dioxide often progressively increases in favor of the former and is, in part, facilitated by the differential solubilities of the two.[33] Ramaswamy[113] used milled (particle size 2 mm) synthetic refuse (25% wood, 50% paper, 25% dog food) to examine the effects of three moisture contents (30, 60, and 80%) on the methane contents of the generated gases. Maximum methane content (58.8% v/v) was found in the presence of a moisture content of 80% with progressive reductions recorded at both 60 (34.6%) and 30% (4.2%). These results were subsequently criticized by Hartz[114] on the grounds that the refuse composition and particle size distribution were not representative.

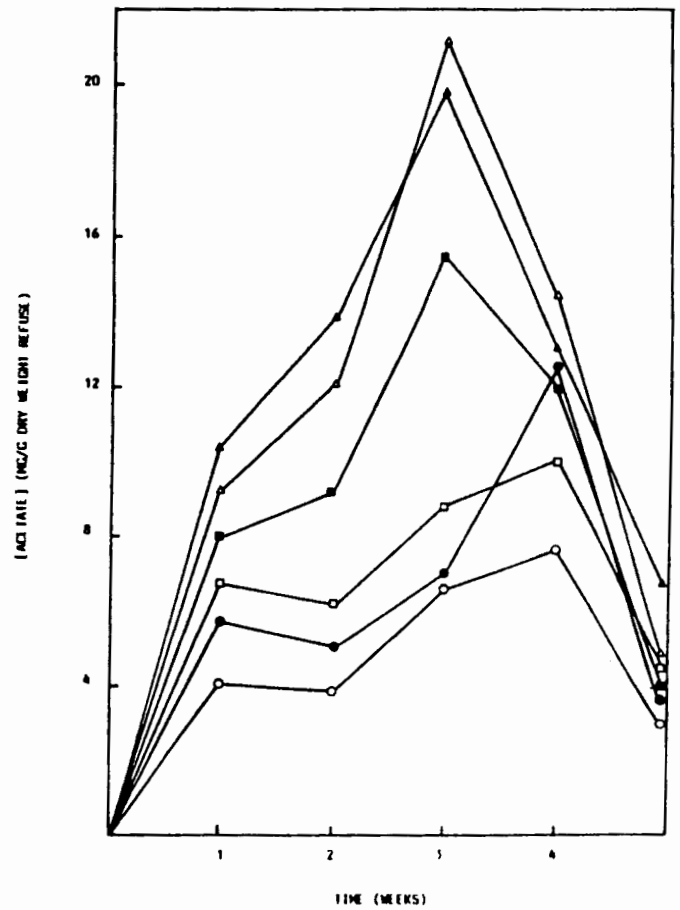

FIGURE 8. Acetate concentration changes in ambient temperature (22 to 27°C, mean 24.2°C) -maintained refuse samples poised at discrete moisture contents of 55 (○), 60 (●), 65 (□), 70 (■), 75 (Δ), and 80% (▲) (w/w).

In particular, the dog food would have provided high nitrogen and phosphorus values compared with typical refuse.

Although it is now generally accepted that controlled water additions may be made to enhance methanogenesis within the refuse mass, it must be recognized that such additions may also introduce problems. For example, rapid infiltration, as discussed earlier, may impede methanogenesis,[103] possibly due to a combination of cooling[77,103,115] and increasing the redox potential which may, in turn, dramatically change the fermentation balance. Although a number of workers[1,96,105] have reported that increased refuse density tends to decrease gas production, the bases of the interactions between moisture content, compaction, and temperature are not clearly understood. Verstraete et al.[96] reported that when refuse moisture contents were raised in increments of 10 up to 65%, the impacts for low density (0.25 t/m^3) were more pronounced than for compacted refuse (0.8 t/m^3) and concluded that these different effects were due to higher

bacterial mobility, which, in turn, promoted hydrolysis and methanogenesis in the former. Conversely, Rees[105] reported that density exerts a differential effect depending on the moisture content of the refuse. Under conditions of a constant moisture content (21%) a density increase from 0.32 to 0.47 ton/m^3 was found to result in a gas production increase from 410 to 845 ml/d/kg dry refuse. Conversely, when the refuse densities were fixed at 0.2, 0.32, and 0.47 ton/m^3, prior to saturation with water, then 2530, 2100, and 1260 ml gas per day per kilogram dry refuse, respectively, resulted. The observed discrepancies in this study were equated with water availability to the microbial species. Subsequently, Ehrig[82] showed that a density increase from 0.7 to 1 ton/m^3 resulted in the absorptive capacity of refuse decreasing from 100 to 24 l/ton.

Finally, Harmsen[55] examined gas production from sites of different ages and found that in a 9-year-old landfill, in which the refuse had been subjected to compaction, methanogenesis had not established, whereas in a 2-year-old site, where compaction had not been practiced, methane production was already evident.

3. Temperature

The effects of temperature elevation on the generation of landfill gas have been examined by a number of workers[1,7,12,77,95,96,116-119] and have been shown to result in gas production increases, particularly over the temperature range of 30 to 35°C.[1] Verstraete et al.,[96] for example, in laboratory model studies, demonstrated that a temperature elevation from 22 to 33°C was accompanied by a gas production rate increase of 70%.

In the refuse mass, the actual temperature attained is determined by a number of factors such as microbial metabolism (aerobic and anaerobic) which, in turn, is directed by the dry density of the emplaced refuse, the specific surface area, the refuse composition and availability of electron acceptors, the landfill water content and temperature, heats of neutralization, and the addition of solar energy, all of which are balanced by heat loss both to the atmosphere and the surrounding soil.[77] Landfill temperature fluctuations in response to long-term air temperature variations have been reported by Rovers and Farquhar.[120] The workers found that in a Canadian (southern Ontario) landfill, the annual average temperature at a depth of 1.22 m was 12°C, with seasonal fluctuations between 2 and 21°C. Perhaps more importantly, it was also shown that even within the psychrophilic range of temperatures methanogenesis occurred.

Rees[45] reported that at the Aveley (U.K.) landfill, which is particularly reactive in terms of methane generation, temperatures at 2.1 m below the surface were not markedly influenced by ambient temperatures during the winter months and remained relatively constant at 25°C. Subsequently, the temperature was shown to rise to 33°C during the summer. At discrete depths of 4.7 and 7.1 m, however, the temperatures continued to rise smoothly by 5°C over the 5-month winter period, to reach a plateau of 43°C during the summer. Thus, it would appear that deep sites are more likely to maintain temperatures favorable for methanogenesis.

Hartz et al.[118] examined the impacts of temperature variations, over the range of 21 to 48°C, on refuse from four different sites. Two approaches were used: short-term residence, with seven different temperatures, and intermediate-term residence, with two temperatures. In this study, the optimum temperature for methanogenesis was recorded at 41°C, and no evolution was detected between 48 and 55°C. Conversely, in anaerobic digesters, methanogenesis has been shown to result at temperatures between 48 and 65°C when the refuse was digested at a solids concentration of <5%.[121,122] Similarly, Zinder et al.[123] demonstrated the thermophilic digestion of municipal refuse in laboratory experiments.

Rees[77] reported that, in temperate climates, in the presence of a refuse moisture content of 55%, sufficient heat could be generated to raise the temperature of the refuse mass above 30°C in a year. Rapid temperature increases are, however, often associated with aerobic metabolism since the succession to anaerobiosis can result in temperature reductions.[12] Merz and Stone[124] used test cells to examine the effects of aeration on refuse temperature profiles and found that in the absence of aeration an initial peak temperature of 43°C was followed by temperature reductions to between 25 and 30°C. In the presence of aeration, however, a temperature peak of 71°C was recorded which subsequently decreased to near 49°C.

A comprehensive laboratory study of the effects of temperature on refuse methanogenesis was made by Kasali.[33] Glass columns, which contained refuse poised at a moisture content of 60% w/w, were used to examine these effects over a period of 14 weeks. At a temperature of 55°C, gas production (mainly carbon dioxide) was apparent during the first 7 d of incubation, although subsequently only extremely low rates of generation were detected. Conversely, although taking somewhat longer to develop, active and continuing gas generations were recorded with the 40°C (4 d), 30°C (3 d), and ambient temperature (14 to 22.5°C) (17 d)-incubated samples. Although the cessation of gas evolution from the 55°C-incubated sample was accompanied by a pH fall from 7.2 to 5.7, reinstatement of a near neutral pH, by the addition of 10% (w/v) sodium bicarbonate, did not result in a resumption of gas generation. In a second experiment, which involved temperature manipulations, Kasali[33] determined that the temperature of 55°C had exerted a time-dependent bactericidal effect. These results were thus in agreement with those of Hartz et al.,[118] who also observed cessation of gas production at 55°C.

Direct comparison of the results of these two studies with those of Pfeffer.[125] Cooney and Wise,[121] and Zinder et al.[123] are, in fact, difficult to make since although similar temperature ranges were used, the last three studies were made at low solids concentrations and with external inocula of methanogens.

Kasali[33] also determined cumulative concentrations of both biogas (Figure 9) and methane (Figure 10) during the incubation period. Although similar trends were obtained for the two, different patterns of gas evolution rates were apparent. Mean biogas evolution rates of 402, 987, and 3020 ml/kg dry refuse per day were calculated for the ambient, 30, and 40°C-incubated samples, which corresponded with methane concentrations of 171, 502, and 1210 ml/kg dry refuse per day.

Although accurate rates of gas evolution *in situ* are difficult to measure, Rees[45] reported values of 323.6 and 126.7 ml/kg/d for total gas and methane, for the Aveley (U.K.) landfill.

The most universal method of recording the effects of temperature on microbiological reactions is by application of the empirical Arrhenius relationship:[126]

$$K = Ae^{-Ea/RT} \qquad (2)$$

Hartz et al.[118] transposed this equation into the logarithmic form, differentiated with respect to temperature, and integrated within the temperature limits to obtain the following:

$$\ln \frac{K_2}{K_1} = \frac{Ea\,(T_2 - T_1)}{R\,(T_2 T_1)} \qquad (3)$$

in which K_2 and K_1 are the methane evolution rates at temperatures T_2 and T_1, respectively, in degrees Kelvin (273 + °C); E_a is the energy of activation, in calories per mole; and R is the gas constant (1.987), in calories per degree Kelvin per mole. The units of K_2 and K_1 are corrected to standard temperature and pressure (STP), cancel with E_a, having units of calories per mole of methane produced at STP. From this equation the workers calculated energy of activation values, indicative of the relative ease of product formation and, therefore, velocity of reaction, for refuse methanogenesis in short- and intermediate-term residence studies. With the former, E_a values of between 22.4 and 23.7 kcal/mol were calculated, whereas for the latter, the corresponding values were between 18.7 and 21.8 kcal/mol. From these results it was concluded that minor temperature changes mediated only minor microbial population shifts.

de Walle and Chian[109] also examined methane recovery from refuse and calculated an E_a value of 14.5 kcal/mol of methane produced, over the temperature range of 17 to 26°C. This

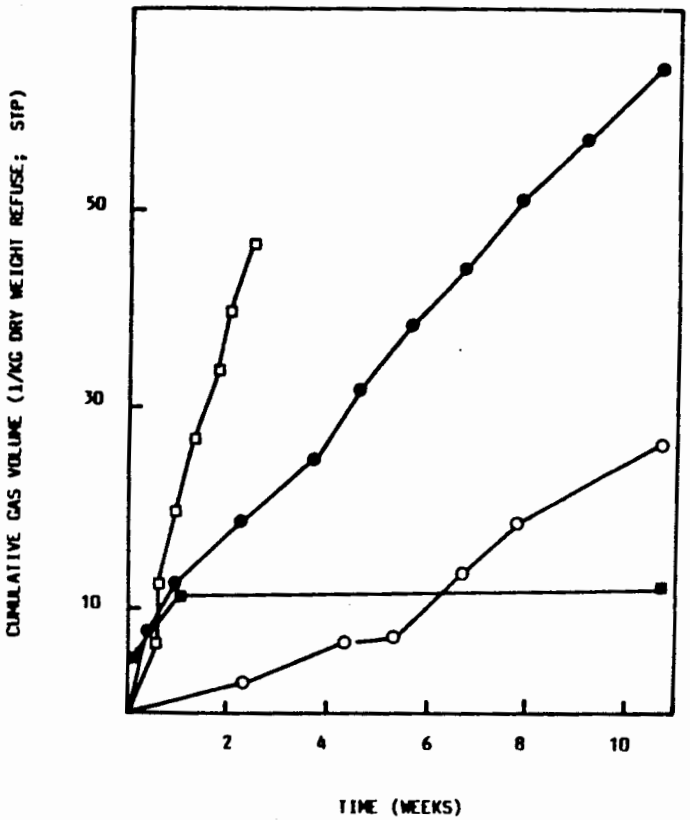

FIGURE 9. Cumulative volumes of gas evolved from laboratory models[33] maintained at ambient temperature (14 to 22.5°C, mean 18.7°C) (○), 30 (●), 40 (□), and 55°C (■). All refuse samples poised at a discrete moisture content of 60% (w/w).

result was in close agreement with the determination of Kasali[33] where an E_a value of 14.8 kcal/mol of methane was recorded for the temperature range of 18.7 to 30°C. In the latter study reaction rate coefficients and Q_{10} values were also reported. Kasali[33] showed that by raising the temperature from ambient (18.7°C) to 30°C the reaction rate constant more than doubled, from 0.07 to 0.17/d, while a further temperature elevation to 40°C resulted in a dramatic increase to 0.51/d. This optimal temperature for methanogenesis was thus in close agreement with the 41°C reported by Hartz et al.[118]

Although over the temperature range of 18.7 to 30°C refuse methanogenesis (Q_{10}, 2.33) was shown by Kasali[33] to behave according to the Arrhenius model, whereby reaction rates double for every 10°C rise in temperature, a second temperature increase, from 30 to 40°C, was accompanied by an approximate tripling (Q_{10}, 2.98) of the rate. These results were, however, in agreement with those of Stuckey,[126] who reported that in methanogenic fermentations the Arrhenius relationship is only valid within a temperature range of 15 to 35°C.

Together with evolution rate changes, temperature increases can also effect dramatic changes in gas composition. Kasali,[33] for example, measured the methane content of a 55°C-incubated

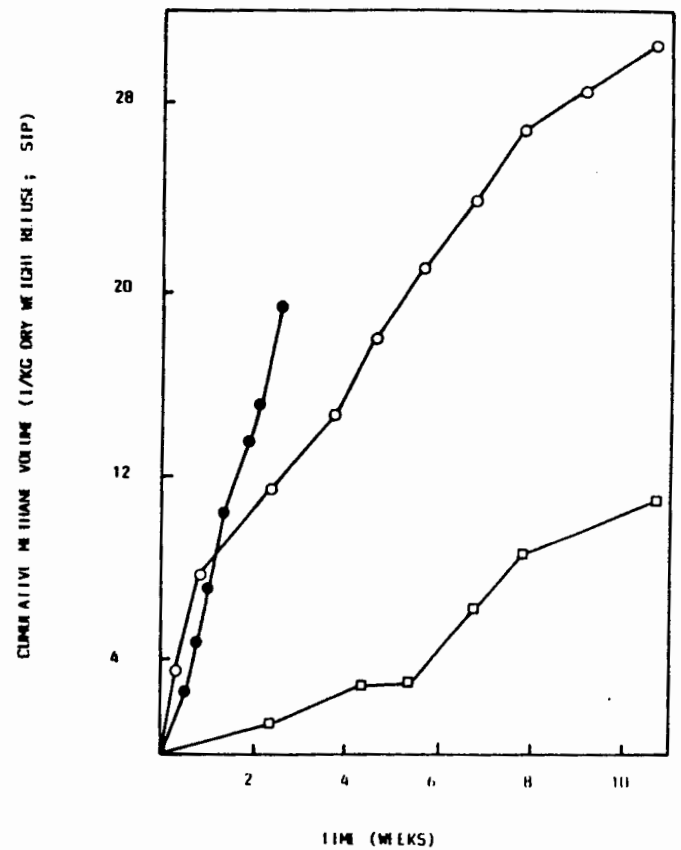

FIGURE 10. Cumulative volumes of methane evolved from laboratory landfill models maintained at ambient temperature (14 to 22.5°C, mean 18.7°C) (□), 30 (○), and 40°C (●). All refuse samples poised at a discrete moisture content of 60% (w/w).

refuse sample at 1.1% (v/v) which was in general agreement with earlier results. However, methane concentrations of 44.6 and 0.9% (v/v) were recorded with temperatures of 35.5 and 45°C, respectively. From these results it is apparent that temperature increases can effect dramatic fermentation balance changes. Kasali[33] examined this phenomenon by incubating refuse samples at ambient (18.7), 30, and 55°C prior to quantitative reduced organic acid analysis. Marked increases in the concentrations of acetic, propionic, *iso*butyric, *iso*valeric, and caproic acids were apparent in the 30°C-incubated refuse compared with the ambient temperature samples, despite comparable final pH values of 7.45 and 7.4, respectively. At an incubation temperature of 55°C, however, dramatic concentration reductions were recorded despite an initial pH fall to 5.7. From these results it was apparent that, although methanogenesis was inhibited at this temperature, acidogenesis was initially operative with the overall concentration reductions accounted for by solventogenesis (methanol, ethanol, acetone, propanol, and butanol).

According to Holt et al.[126] batch solventogenic fermentations of carbohydrate-containing

media by *Clostridium acetobutylicum*, characteristically, proceeds in two distinct phases. In the first (acidogenic) phase, carboxylic acids are produced, which mediate pH reductions, while in the second (solventogenic) phase, solvents are produced and, as a consequence, the pH rises. The results of Kasali[33] also suggested a similar two-phase fermentation pattern.

4. pH and Alkalinity

In refuse, although methanogens play key roles, both direct and indirect, in the removal of the products of acidogenesis, they are present in very low numbers in recently emplaced material. As a consequence, high initial fermentative activity can lead to the accumulation of high concentrations of reduced organic acids which lower the pH to the detriment of the methanogens. This pH can, however, in many instance, be obviated by the microbial generation of buffering capacity. Carbon dioxide, for example, which is an end product of both aerobic and anaerobic mineralization, plays an important role in the buffering of refuse due to its solubilization to form carbonic acid. In the presence of alkaline earth carbonates, which may be present in the sealing soils, carbonic acid reacts to form alkaline earth bicarbonates and, in the presence of iron, iron bicarbonates, thus resulting in an increase in alkalinity.

Other microbiological reactions which may contribute to the buffering capacity of refuse are the reduction of sulfate to hydrogen sulfide, and the reduction of nitrate to nitrogen or ammonium. For both these reductive processes carbon dioxide is also generated. Sulfate reduction can lower the pH due to the concomitant generation of H^+:

$$SO_4^{2-} + 2CH_2O \rightarrow HS^- + 2HCO_3^- + H^+ \qquad (4)$$

Conversely, the production of NH_4^+ provides a sink for H^+, and this prevents the establishment of an acidic environment.[130] Since nitrate reduction is energetically more favorable than sulfate reduction,[131] then, on an equivalence basis, the former process should dominate.

a. pH

Bookter and Ham[132] determined the pH values of refuse samples obtained from test lysimeters of known age and compared these with freshly shredded material. Average pH values of 6.9, 6.9, 4.4, and 5.3 were recorded for fresh, 1, 6, and 9-year-old refuse samples, respectively. Of these, methanogenesis was apparent in the 1-year-old refuse, while the 6-year-old sample had an erratic history of methane production and manifested a pungent odor of hydrogen sulfide. Unfortunately, no data were reported of methanogenesis of the 9-year-old refuse.

Rovers and Farquhar[120] also used test cells to examine the effects of excessive infiltration on gas production and found that although carbon dioxide was produced, methane was not. Initially, the pH remained near 6.0, but later fell to 5.5 and was accompanied by reductions in both bicarbonate alkalinity and ammonium ion concentration.

Kasali[33] used laboratory refuse columns (fitted with gas collection systems), poised at initial discrete gross pH values, by the addition of deoxygenated phosphate buffer to moisture field capacity (78.8%), to examine the effects of pH on refuse methanogenesis at 30°C. Corresponding anaerobic cultures were also initiated in closed bottles to examine solvent and carboxylic acid metabolisms. In all, five discrete pH values, 5.3, 6.2, 7.4, 7.7 (distilled water control), and 8.3 were used. The choice of a phosphate buffering system was made after first establishing that the refuse was not phosphorus limited.

During the first 2 weeks of fermentation, total gas evolution rates increased as the initial pH of the refuse increased; thus, maximum rates were observed at a pH of 8.3, while the lower rates were recorded for pH values of 6.2 and 5.3 (Figure 11). As the fermentation progressed, however, dramatic changes became apparent. Thus, with the exception of the control and, to a lesser extent, the sample poised at pH 6.2, where gas evolution rates continued above the initial rates, declining rates became apparent. Kasali[33] also measured the total volumes of gases

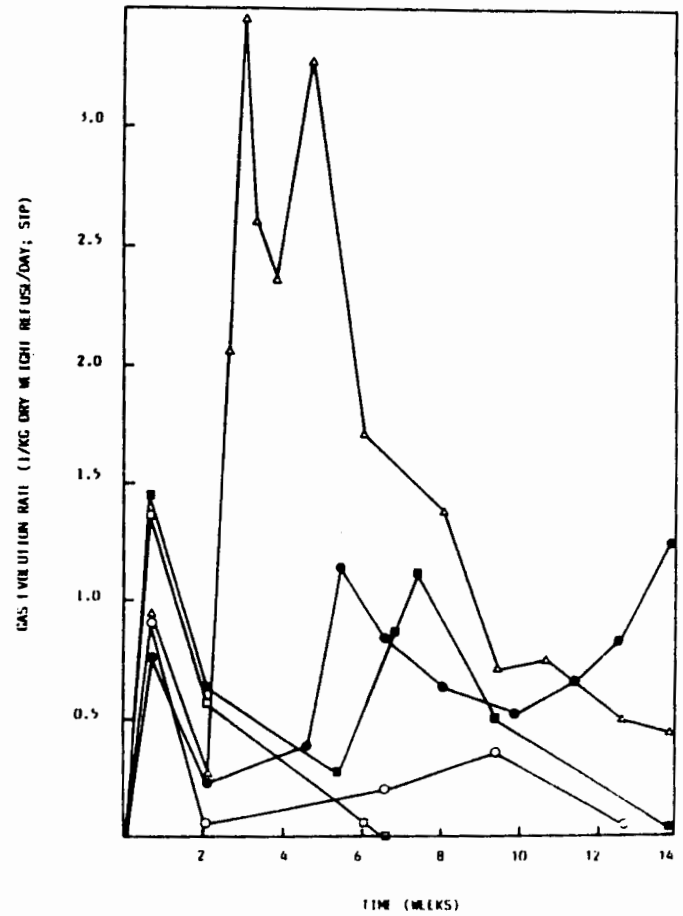

FIGURE 11. Gas evolution rate changes from 30°C-maintained laboratory landfill models in which refuse samples poised at discrete pH values of 5.3 (○), 6.2 (●), 7.4 (□), and 8.3 (■), by 0.2 M phosphate buffer additions, and 7.7 (△) by glass-distilled water additions to refuse field capacity (78.8%).

evolved and found that they were in the order pH 7.7 (103.4), 6.2 (66.8), 8.3 (41.5), 5.3 (2[illegible]) and 7.4 (16.3 l/kg dry refuse).

The trends in the rates of methane evolution (Figure 12) were very similar to those of the total gas with maxima and minima recorded at pH values of 7.7 and 7.4, respectively. Perhaps not surprisingly, the least methanogenic sample exhibited the highest concentration of carboxylic acids, while the most methanogenic sample had the lowest concentration. Unlike the rates of total gas evolution, however, with the exception of the pH 7.4-poised sample, the rates of methane evolution progressively increased to levels which were higher than those observed during the first 2 weeks of incubation before subsequently declining. It is interesting to note, however, that at the end of the incubation period the highest rate of methanogenesis was recorded

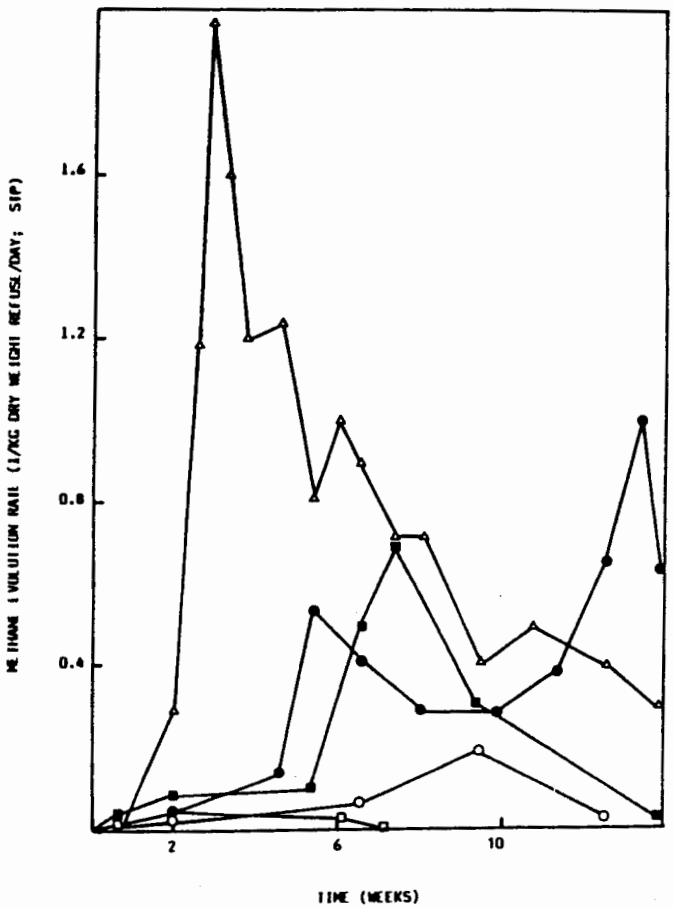

FIGURE 12. Methane evolution rate changes from 30°C-maintained laboratory landfill models[33] in which refuse samples poised at discrete pH values of 5.3 (○), 6.2 (●), 7.4 (□), and 8.3 (■), by 0.2 *M* phosphate buffer additions, and 7.7 (Δ) by glass-distilled water additions, to refuse field capacity (78.8% w/w).

with the pH 6.2-poised sample, although at this point the gross pH had risen to pH 7.3. Once again the total volumes of methane evolved followed the same pattern as the total volumes of gases. The percentage methane contents of the evolved gases were also affected by the set pH values and, in addition, were found to vary with time in all samples. As would be anticipated, for all samples the lowest percentage concentrations of methane were present during the initial stages of fermentation, while the highest were recorded at the end of the incubation period. Although dramatic variations were seen in the methane contents of the evolved gases from each of the five treatments, the average percentage methane contents followed the pattern established for the total volumes of gases and component methane, with the maxima and minima recorded at pH values of 7.7 and 7.4, respectively.

Time course profiles of carboxylic acid metabolism in the same refuse samples showed that

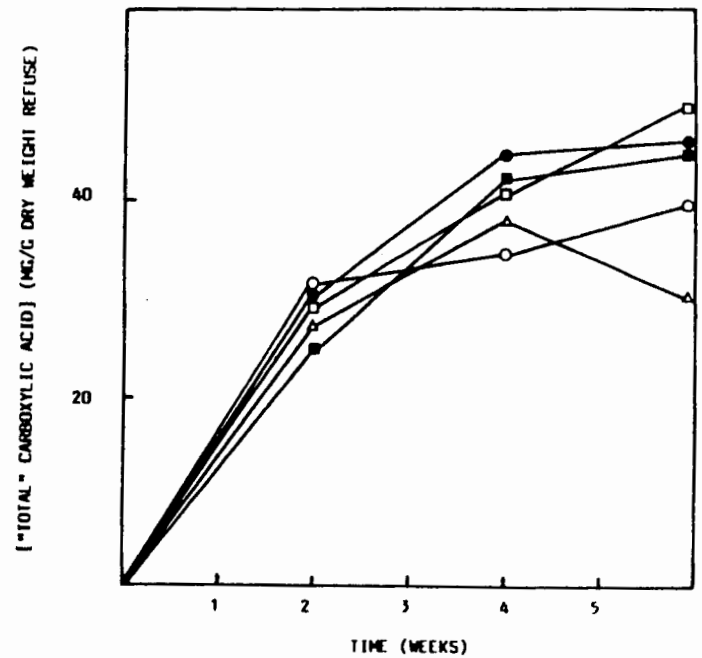

FIGURE 13. Changes in concentrations of "total" organic acids (acetate, propionate, *iso*-butyrate, butyrate, *iso*valerate, valerate, caproate) at 30°C in refuse samples poised at discrete pH values of 5.3 (○), 6.2 (●), 7.4 (□), and 8.3 (■), by 0.2 *M* phosphate buffer additions and 7.7 (Δ) by glass-distilled water addition, to refuse field capacity (78.8% w/w). All concentrations corrected by subtraction of time-zero concentrations.

in the first 2 weeks of the fermentation, maximum concentrations were recorded in the samples poised at the lower pH values (Figure 13). As the fermentation entered the fourth week, however, this pattern changed until, by the sixth week, the "total" carboxylic acid content was highest in the samples poised, initially, at pH 7.4, while the lowest "total" concentration was detected in the control samples. Although comparison of Figures 12 and 13 shows that at corresponding discrete times there was an approximate inverse relationship between methanogenesis and "total" carboxylic acid concentrations, direct analogies cannot be made since the latter represent a balance between acidogenesis and acidotrophy.

As a consequence of this, time-course profiles of individual reduced organic acids are difficult to interpret, although some interesting observations were reported. For acetate, after the first 2 weeks of fermentation, the highest concentrations were recorded in the initially neutral- or alkaline-poised samples. For propionate, however, the detected concentrations appeared to partition themselves with respect to pH. Essentially, the highest concentrations were recorded with the pH 7.4- and 8.3-poised samples. Intermediate concentrations were detected in the pH 6.2 and control samples, while the lowest concentrations were recorded with the pH 5.3-poised refuse. These groupings were, in fact, maintained throughout the incubation period which led Kasali[33] to speculate that propionate metabolism was a function of propionogenesis which was strongly influenced by the initial pH value. Examination of the butyrate profiles showed that during the first month of fermentation the control and pH 6.2-poised samples, which exhibited methanogic activities during this period, were characterized by high concentrations of this acid.

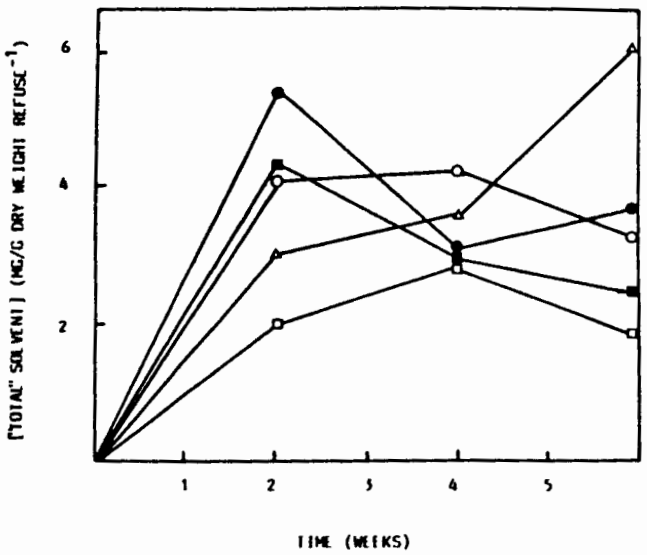

FIGURE 14. Changes in concentrations of "total" solvents (acetone, methanol, ethanol, propanol, *iso*propanol, butanol) at 30°C in refuse samples poised at discrete pH levels of 5.3 (○), 6.2 (●), 7.4 (□), and 8.3 (■) by 0.2 *M* phosphate buffer addition, and 7.7 (Δ) by glass-distilled water addition, to refuse field capacity (78.8% w/w).

For caproate, in general, the higher concentrations were recorded with the samples poised at the lower pH values. Finally, very little quantitative variations, with respect to pH, were found for *iso*butyrate and *iso*valerate, and, with the exception of the pH 8.3 treatment, a similar picture emerged with valerate.

Kasali[33] also examined the influence of pH on alcohol and ketone metabolism in domestic refuse. After an incubation period of 14 weeks, although no alcohols or ketones were detected in the pH 5.3, 6.2, and control samples, acetone (0.95 mg/g dry refuse) and propanol (4.54 mg/g dry refuse) were detected in the pH 7.4 and 8.3 samples, respectively. Kasali[33] then monitored time-course profiles of the individual alcohols (ethanol, methanol, butanol, propanol, and *iso*propanol) together with acetone over a time period of 6 weeks. Summation of these individual concentrations showed that after an incubation period of 2 weeks, the total solvent concentrations decreased in the following order of the initial pH values: 6.2, 8.3, 5.3, control, and 7.4 (Figure 14). This pattern, however, changed by the fourth week until, by the sixth week of incubation, the total solvent concentrations decreased in the following order: control, pH 6.2, 5.3, 8.3, and 7.4. Throughout the 6-week study, comparatively the lowest total concentrations of solvents were systematically detected in the pH 7.4-poised samples. From this study, as a consequence of the presence of solvents in all the samples assayed, together with qualitative and quantitative changes observed in response to changes in initial pH, the speculation was made that solventogenesis was an important carbon and electron flow pathway in the overall refuse fermentation.

Of the six solvents detected, only ethanol and propanol were present in every sample, particularly in the samples poised initially at acidic and alkaline pH values. Conversely, butanol and methanol were detected only in the pH 5.3 and 6.2 samples, while acetone was present only in the control and pH 7.4 samples. Finally, with the exceptions of the control and pH 8.3 samples, the remaining samples were found to contain *iso*propanol.

According to Datta and Zeikus,[133] the production of acetone offers the organism a mechanism for recycling coenzyme A (CoA) without using reduced nucleotides or generating protons. Thus, when the reduced nucleotide pool is increased in proportion to CoA, the organism switches away from the acetone pathway in favor of, for example, ethanol and butyrate generation. In the presence of near-neutral pH regimes, optimal glycolysis is favored. Consequently, optimal growth of the neutrophilic solventogens results, thus, possibly, mediating CoA recycling through acetone production.

In the acetone-butanol-ethanol fermentation, between 75 and 78% of the electrons in the carbohydrate substrate are found in the solvents, of which butanol accounts for between 50 and 55%. Of the remainder, the nonsolvent products (cells, hydrogen, acetate, and butyrate) account for between 20 and 25%, with the major portion of these (11 to 15%) in the form of hydrogen gas.[133] Thus, of all the reduced end products, butanol production requires the presence of the most reduction energy.

From the overall results of Kasali's study,[33] it was apparent that pH treatments mediated a two-phase response in the refuse methanogenic fermentation. In the initial phase, the rates of methanogenesis increased as the applied pH increased. This trend, however, drastically changed during the subsequent phase(s) of the fermentation as acidogenesis and solventogenesis continued to exhaust the buffering capacities of the applied pH treatments.

In an actual landfill, Rees[45] recorded a transient accumulation of fatty acids, at an approximate concentration of 5000 mg/dm^3, in conjunction with a pH of 5.4. Since this site was methanogenically active, however, within a period of 2 months the pH progressively rose to 8.4 with a concomitant reduction in the fatty acid concentration to <20 mg/dm^3. These data were taken to indicate that an active and well-established methanogenic population could tolerate and function at much lower pH values in the landfill ecosystem than they could either in monoculture or in full-scale anaerobic sewage sludge digesters.

Despite the absence of definitive studies of the specific effects of pH on the interrelated processes of methanogenesis, solventogenesis, and acidogenesis in refuse, speculations may be made on the mechanisms operative.

It is now recognized that high concentrations of carboxylic acids and low pH regimes can inhibit methanogenesis in anaerobic digestion processes,[illegible] although the mechanism and the quantitative aspects of this are not fully resolved. Weak acids, such as carboxylic acids, diffuse rapidly through microbial membranes[134] according to the pH. When added in large volumes, however, these acids dissipate the ΔpH by acting as uncoupling agents or protonophores. In neutrophilic anaerobic bacteria the internal pH is maintained more alkaline than the medium, although pH reductions are seen as the external pH becomes more acidic. As a consequence of this reduced internal pH, inhibition of pH-sensitive cellular reactions results, and, thus, growth and fermentation cease.[111]

Jarrell and Sprott[135] examined the effects of external pH on the intracellular pH of two neutrophilic methanogens, *Methanospirillum hungatei* GP1 and *Methanobacterium thermoautotrophicum*, and found that under a neutral external pH regime, no transmembrane pH gradient existed. When the external pH was reduced below neutrality, however, the originally alkaline intracellular pH was found to decrease. The workers also examined cytoplasmic penetrations of propionate and butyrate in the presence of external pH regimes of 5.8, 6.5, and 8.0 and found highest internal concentrations at pH 5.8 with total absence at pH 8.0. Conversely, methylamine penetration was apparent for each of the three discrete pH values. From these results it may be concluded that the ability of carboxylic acids to influence the intracellular pH, and, thus, the metabolic activity of methanogens, depends first and foremost on their potential to penetrate the cells. This penetration, in turn, depends on both the affinity of the methanogens for the specific carboxylic acid(s) and the pH of the microniche. If it is assumed that the toxicity of carboxylic acids to methanogens is, essentially, due to the acidification of the microbial cytoplasm, then of all the carboxylic acids generated in refuse, acetate, as a major methanogenic substrate, should

exert the most predominant toxic effect at all possible pH values. In landfill, acetic acid is quantitatively the major carboxylic acid.[44,45] Accumulation of carboxylic acids, with a resultant lowering of pH, has been shown to first slow and then inhibit acidogenesis in refuse.[110] In anaerobic ecosystems where methanogens are active, however, end product inhibition of acidogenesis does not occur because a favorable pH for the acidogens is maintained by the methanogens which utilize acetate and facilitate the dissimilation of other carboxylic acids by serving as electron sinks for acetogenic proton-reducing bacteria.[56]

In addition to the pH changes mediated by the interactions between methanogens and acidogens, solventogens also play key integral roles, since it has been suggested[136] that solventogenesis, which involves the formation of neutral molecules from acids, is a neutralization mechanism which is triggered when the environmental pH falls.

The activities of solventogenic organisms in batch anaerobic fermentations may be divided into two phases. In the first, rapid growth results in the formation of organic acids, and the pH declines. In the second phase, solvents are formed at the expense of further substrate consumption, and, in part, the acids formed. The net results are a small increase of pH and, ultimately, cessation of growth.[137] Although the factors of solvent synthesis in this latter stage are not fully defined, it may be speculated that

1. Low pH
2. Toxicity of high concentrations of acids
3. Inducement of a shift from a high energy conservation efficiency in ATP formed to a much lower value of that efficiency
4. A high partial pressure of gaseous hydrogen[137]

are all key components. According to Roos et al.,[138] solventogenesis is predominantly regulated by the availability and demand for biosynthetic (ATP) and reduction ($NADH_2$) energy.

Anaerobic solventogenesis is a characteristic of neutrophilic clostridia[138] which are stressed by both acidic and alkaline pH regimes and, as a consequence, necessitate ATP-dependent maintenance of a pH gradient. Thus, pH values outside the optimal range for metabolism and growth impose an additional ATP demand. According to Jöbses and Roels,[137] the switch from acidogenesis to solventogenesis may be indicative of failure of the acetogenic metabolic pathway, which is the most efficient from the point of view of ATP generation, to provide sufficient energy dissipation for growth. Although the microorganisms and mechanisms involved in the degradation of solvents in landfill are not yet known, a number of reports have been made on other anoxic ecosystems. Thus, it has been shown that in addition to methanogenesis, discussed earlier, methanol may be converted to acetic acid, by species of *Clostridium*, or to acetate, butyrate, and caproate, by *Eubacterium limosum*.[139,140] However, it is not yet known whether the non-methanogenic species or the methanogens are the stronger competitors.

In anoxic freshwater sediments *Desulfovibrio* spp. have been shown[141] to be the predominant ethanol-degrading bacteria. In this ecosystem *Desulfobulbus propionicus* was shown to ferment ethanol to propionate and acetate, while propanol and butanol were converted to propionate and butyrate, respectively. From these results, it is apparent that alcohols are primarily converted to fatty acids, and, as such, both the production and subsequent degradation of the solvents are likely to cause pH fluctuations in anoxic ecosystems.

Once again, the partial pressure of hydrogen is an important determinant of degradation. Thus, for example, the dissimilation of ethanol is energetically favorable at a partial pressure of approximately 0.15 atm, while the corresponding degradations of reduced organic acids such as butyrate and propionate require partial pressures of 2×10^{-3} and 9×10^{-5} atm, respectively.[142]

b. Alkalinity

In the eventuality that high initial fermentative activity results in the accumulation of reduced organic acids in refuse, an overall fermentation deceleration may then be mediated.[55,98,143] In order to establish a stable methanogenic fermentation in refuse it has, therefore, been suggested[45,97] that buffering substances such as lime, calcium carbonate, and sodium bicarbonate should be added. This is, perhaps, not surprising since leachate from an acidogenic-phase landfill has been shown to have a pH of 5.7 and a bicarbonate content of 17 mg/l, while corresponding values for methanogenic-phase leachate were 7.0 and 12,000 mg/l.[55] Sodium bicarbonate additions have been used to maintain favorable pH values in fermenting refuse samples and, as a consequence, increase gas production.[1,144] Ehrig[82] also examined the effects of alkalinity on gas production from refuse and reported that an acetic acid:alkalinity ratio <0.8 was required before methanogenesis was initiated.

In addition to neutralization, alkali additions, which may represent significant cost factors,[45] may also result in alterations to the chemical structures and composition of refuse components.[145] Thus, for example, in the presence of calcium carbonate, methanogenesis has been shown to increase[97] due to a combination of pH elevation in conjunction with a precipitation of potentially toxic heavy metals.[146]

Kasali[33] used 30°C-maintained laboratory columns (fitted with gas collection systems) which contained refuse supplemented with deoxygenated sodium bicarbonate (1, 2.5, or 5% w/v) to field capacity moisture content (77% w/w) to examine the influence of this chemical on refuse methanogenesis. Corresponding anaerobic cultures were also initiated in closed bottles to examine the effects of sodium bicarbonate on acidogenesis. The initial pH values of the solutions used (1, 2.5, and 5%) were 8.8, 8.5, and 8.3, respectively, although after addition the gross pH values of the refuse were 7.2, 7.3, and 7.7, respectively. A distilled water control (pH 7.0) was also included which resulted in a refuse pH of 7.1. The observed pH reductions as the concentration of sodium bicarbonate was increased may be accounted for by increased carbonic acid formation as the bicarbonate concentrations of the solutions increased:

$$NaHCO_3 \rightarrow Na^+ + HCO_3^- \quad (5)$$

$$HCO_3^- + H_2O \rightarrow H_2CO_3 + OH^- \quad (6)$$

$$HCO_3^- \rightarrow CO_3^{2-} + H^+ \quad (7)$$

Refuse supplementation, however, could possibly have resulted in an interaction between the carbonic acid and the refuse carbonates, and, thus, bicarbonate formation. General consumption of this bicarbonate alkalinity would, thus, have effected a pH reduction.

Gas evolution was monitored over a period of 92 d, and it was found that in the presence of sodium bicarbonate additions (1, 2.5, and 5% w/v solutions), the total volumes of gases evolved increased by factors of 2.5, 3.2, and 1.5, respectively, compared with the distilled-water control. Of these, however, only the first two concentrations effected methane volume increases. Although these results possibly indicate that 5% (w/v) sodium bicarbonate exerts a differential effect on methanogenesis and acidogenesis, it is also possible that a component of the gas evolved was chemically derived:

$$NaHCO_3 + H^+ \rightarrow Na^+ + H_2O + CO_2 \quad (8)$$

This possibility appeared to be supported, in part, by the gas composition data, which showed that the average methane contents of the evolved gases were 53.5, 70.3, 71.4, and 42.7%, which corresponded to sodium bicarbonate concentrations of 0, 1, 2.5, and 5% w/v, respectively. These concentrations were, however, somewhat lower than the 88% recorded by Ghosh.[110]

For each of the three sodium bicarbonate treatments, during the first 6 weeks of incubation, gas evolution rates were generally higher than the control, and it was only after this point that in the presence of the 5% solution, deceleration was evident (Figure 15). A similar picture was

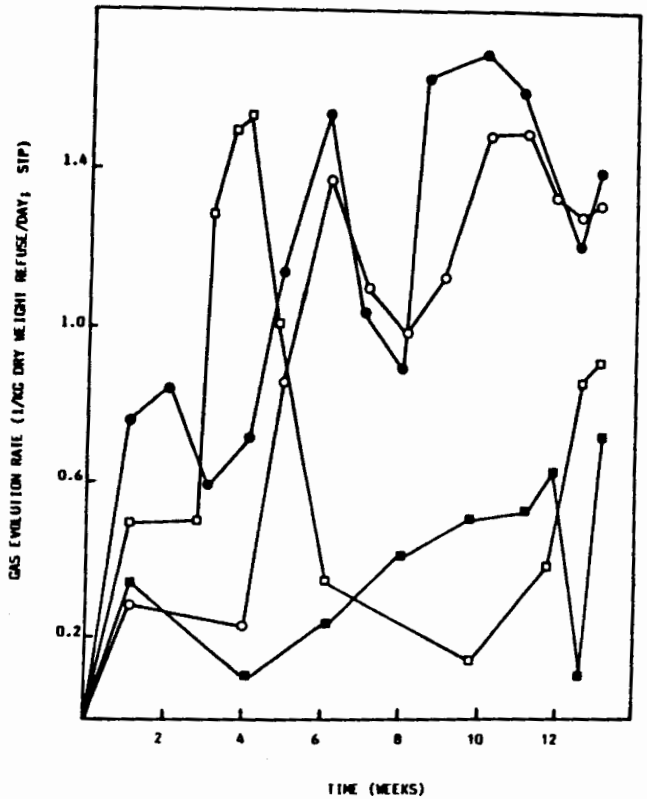

FIGURE 15. Gas evolution rate changes from 30°C-maintained laboratory landfill models[33] in which refuse moisture contents adjusted to field capacity by addition of 1 (○), 2.5 (●), and 5% (□) (w/v) sodium bicarbonate solutions, and glass-distilled water (■).

also apparent for methanogenesis (Figure 16). The calculated geometric means of the methane evolution rates were 0.1, 0.51, 0.62, and 0.12 l/kg dry weight per day for the 0, 1, 2.5, and 5% sodium bicarbonate-treated samples, respectively.

During the course of the experiment, fluctuations were seen in the potentially inhibitory effects of the 5% sodium bicarbonate-supplemented sample, possibly as a consequence of chemical changes mediated by acidogenesis. A possible factor here was the presence of sodium ions, since it has been shown[147] that at a concentration of 14 g/l, a 50% reduction in refuse methanogenesis was effected.

In the study of Kasali[33] the concentration of sodium ions added, in excess of background refuse concentrations, approximated to 14.5 g/l. Thus, since acidification of refuse by carboxylic acids increases the ionic strength, it would be expected that as acidogenesis progressed the ionization of refuse sodium salts should have increased, thus leading to a general increase in the total concentration of free sodium ions. In this eventuality, refuse cation toxicity would be regulated by the concentrations of carboxylic acids.

Partial support for this hypothesis was gained from the observation that inhibition of methanogenesis was coincident with total carboxylic acid concentration increases in the 5%

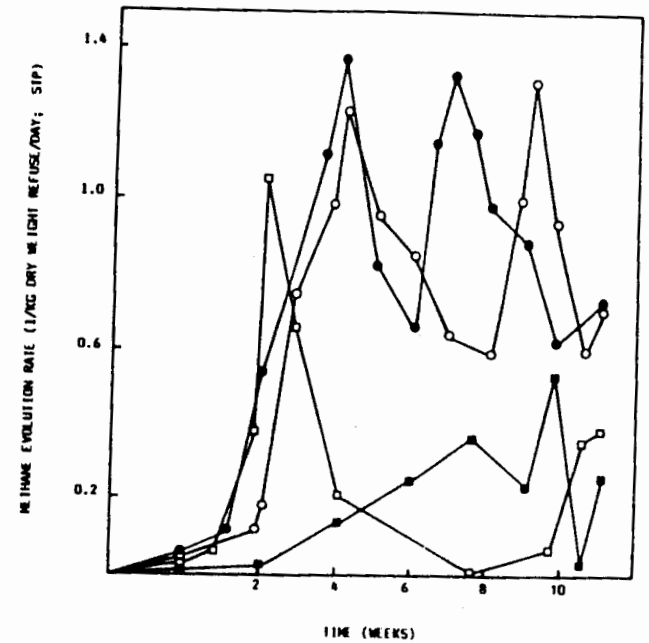

FIGURE 16. Methane evolution rate changes from 30°C-maintained laboratory landfill models[33] in which refuse moisture contents adjusted to field capacity by aaddition of 1 (○), 2.5 (●), and 5% (□) (w/v) sodium bicarbonate solutions, and glass-distilled water (■).

sodium bicarbonate-supplemented samples (Figure 17). Results from actual landfills, however, have shown that methanogenesis was the major process controlling acidotrophy.[54,55] Thus, any determination of the effects on sodium bicarbonate additions could best be made during the early stage of the refuse fermentation when methanogenesis was minimal. From Figure 17 it can be seen that during this phase, acidogenesis was inhibited in the presence of 5% sodium bicarbonate. With time, however, the total concentrations of acids rose, and these were at the expense of methanogenesis.

Kasali[33] also examined the concentrations of individual reduced organic acids (acetate, propionate, butyrate, *iso*butyrate, *iso*valerate, valerate, and caproate) during the course of the fermentation. In the first 2 weeks highest acetate concentrations were detected in the 1 and 2.5% sodium bicarbonate-supplemented samples, which suggested that the alkali enhanced acetogenesis. Once again the concentration of sodium bicarbonate appeared to be critical since inhibition was seen in the presence of the 5% solution. As the fermentation continued, however, progressive increases in the concentration of acetate were apparent, which suggested that the rate of acetogenesis was faster than the rate of acetotrophy. This pattern was not repeated with propionate since throughout the course of the experiment the highest concentrations were detected in the 1%-supplemented samples followed by the 2.5%, coincident with the highest rates of methanogenesis. For butyrate, increased concentrations were, in general, recorded in the presence of increased methanogenic activity. This was, perhaps, not surprising since butyric acid bacteria also produce hydrogen, and, as such, butyrate production would be expected to be profoundly influenced by the partial pressures of hydrogen in the samples. Similar patterns of increased concentrations of acids in the presence of elevated rates of methanogenesis were also apparent for *iso*butyrate, *iso*valerate, valerate, and caproate.

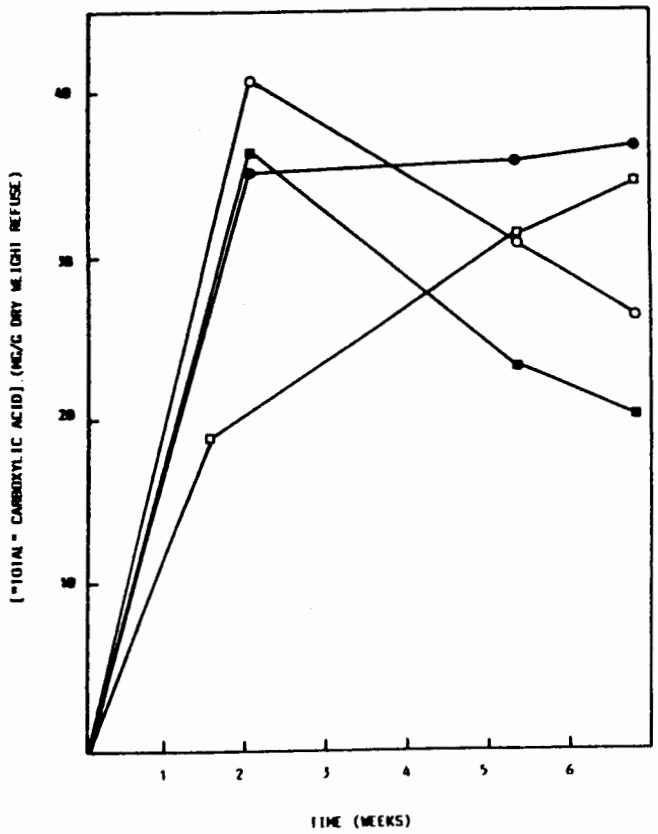

FIGURE 17. Changes in concentrations of "total" volatile fatty acids (acetate, propionate, *iso*butyrate, butyrate, *iso*valerate, valerate, caproate) at 30°C in refuse samples adjusted to moisture field capacity by addition of 1 (○), 2.5 (●), and 5% (□) (w/v) sodium bicarbonate solutions, and glass-distilled water (■). All concentrations corrected by subtraction of time-zero concentrations.

Finally, Kasali[33] determined the gross pH values of the refuse columns after a total incubation period of 92 d and recorded values of 8.0, 8.3, 7.9 and 7.2 for the 1, 2.5, and 5% sodium bicarbonate and distilled water-treated samples, respectively. Since these pH values were higher than the initial pH values of the samples, Kasali[33] concluded that the refuse was capable of generating additional alkalinity as the fermentation progressed. In addition to refuse columns the importance of alkalinity has also been demonstrated in completely stirred tank reactors maintained under anoxic conditions.[148] In these fermenters highest gas yields were recorded with an alkalinity of 16 g $CaCO_3$ per kilogram total solids. From the results of this study it was concluded that in the presence of low alkalinity, fatty acids would accumulate at the expense of methane.

5. Role of Hydrogen

Although optimization of refuse methanogenesis by hydrogen control is not, as yet, a realistic option, it is worth considering the important role of this election donor. In anaerobic environ-

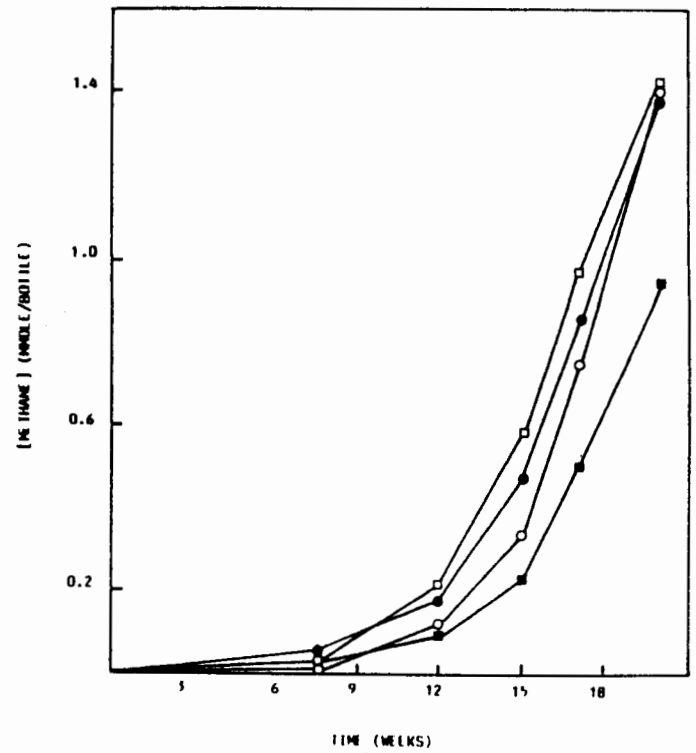

FIGURE 18. Changes in concentrations of methane evolved in the presence of initial gas head spaces of oxygen-free nitrogen (○), hydrogen (●), H_2/CO_2 (80:20) (□), and $H_2/CO_2/N_2$ (10:5:85) (■).

ments where methanogenesis occurs, hydrogen is rarely detected despite the presence of large numbers of hydrogen-producing organisms.[149] From metabolic studies, which involved the coupling of methanogens with hydrogen-producing bacteria, the concept of interspecies hydrogen transfer was developed whereby molecular hydrogen was thought to pass from hydrogen-producing species to methanogens.[50] Although, theoretically, the terminal methanogenic step could be the key rate-controlling process in anaerobic decomposition, microbiological investigations have shown that sulfate reducers consume hydrogen in sulfate-containing environments and, as a consequence, limit the availability of this substrate to methanogens.[51] Thus, the presence of hydrogen in anoxic ecosystems can invoke various reactions which could inhibit or stimulate methanogenesis.

Kasali[33] used sealed bottles, which continued pulverized refuse of 55% (w/w) moisture content, to examine the effects of hydrogen, either alone or in combination with other gases, on refuse methanogenesis and acidogenesis at 30°C. In all, four gases/gas mixtures were used: $H_2/CO_2/N_2$ (10:5:85); H_2/CO_2 (80:20); H_2; and oxygen-free nitrogen (OFN).

After the first week of incubation, all the hydrogen-supplemented samples exhibited stimulation of methanogenesis in comparison with the OFN-treated controls (Figure 18), thus agreeing with the results of a similar study made with lake sediment.[151] The apparent stimulations of methanogenesis in presence of 80 and 100% H_2 continued until the twentieth day, at which point comparable concentrations were also recorded with the controls. A possible

explanation for this could be found if the added hydrogen stimulated methanogenesis from H_2/CO_2, but inhibited methanogenesis from acetate which was assumed to be the key methanogenic substrate in the control samples. Due to acetogenesis in the refuse, the acetate pools should have increased with time and, as a consequence, effected increased rates of methanogenesis. In the hydrogen-supplemented samples, however, the hydrogen concentrations should have decreased with time, thus limiting the rates of methanogenesis from H_2/CO_2. Labeling studies[31] have, in fact, shown that carbon dioxide was rapidly reduced to methane in the presence of hydrogen with little acetate used before hydrogen exhaustion. Although it may be speculated that the addition of hydrogen to acetogenic samples should have resulted in the accumulation of acetate, Kasali[33] found no evidence of this. According to Wolin,[152] the theory of interspecies hydrogen transfer predicts that under conditions of high partial pressures of hydrogen, anaerobic metabolism is altered such that the fermentation is characterized by a decrease in substrate utilization, an increase in concentrations of reduced fermentation products such as propionate and longer-chained fatty acids, and a decrease in the concentrations of oxidized end products such as acetate. The results of Kasali[33] were in agreement with these predictions since both propionate and hexanoate accumulated in the hydrogen-supplemented samples, although the concentrations decreased with increasing concentrations of hydrogen. These results, therefore, suggested that the increased concentrations of hydrogen inhibited the generation of reducing equivalents within the samples. Evidence for this possible inhibition of glycolysis was found with the acetate concentrations, which decreased as the concentrations of hydrogen increased.

Thus, it appeared that high concentrations of hydrogen inhibited both methanogenesis from acetate and heterotrophic acetogenesis. The inhibition of glycolysis should have resulted in a reduced rate of carbon dioxide production. Thus, it may be speculated that in the presence of 100% hydrogen, which exhibited the lowest glycolytic activity, the rates of methanogenesis from H_2/CO_2 were limited by the decreased production of carbon dioxide. Figure 18 does, in fact, show that in comparison with the H_2/CO_2 (80:20)-treated samples, the 100% hydrogen-treated samples exhibited decreased productions of methane.

Figure 18 also shows that, in comparison with the control samples, methanogenesis was reduced in the presence of $H_2/CO_2/N_2$ (10:5:85). The 2:1 ratio of H_2/CO_2 offers a possible explanation for this since the production of 1 mol of methane from H_2/CO_2 requires the reduction of 1 mol of carbon dioxide by 4 mol of hydrogen. Thus, it would be anticipated that hydrogen exhaustion would have resulted in excess carbon dioxide, particularly if this gas was also generated, which, in turn, would have inhibited methanogenesis from acetate.[153]

In addition to these possibilities, sulfate reduction could also have been operable. However, since the samples were found to have a mean total sulfur content of 0.04 mmol/g dry weight, it is unlikely that their effects were significant. Although in sediments low in sulfate, sulfate-reducing bacteria have been shown to degrade propionate and longer-chained fatty acids to acetate,[154] similar results were not reported by Kasali.[33] In this latter study the major influence of hydrogen was on the methanogens, which led Kasali[33] to speculate that methanogenesis was the major hydrogen sink in anaerobic refuse metabolism.

6. Effects of Carbon Dioxide and Methane

The inhibition of microbial metabolism by fermentation end products is well documented.[155] Thus, for example, it has been reported that refuse acidogenesis and methanogenesis are inhibited by a combination of high concentrations of carboxylic acids and the resultant low pH values.[45,110] However, although the labile carbon fraction of refuse is ultimately mineralized to carbon dioxide and methane, the influence of these two gases on the refuse fermentation has received little attention. It is apparent that carbon dioxide and methane both flux out of landfill, provided that the gas pressure in the refuse mass exceeds the atmospheric pressure, although the thickness and permeability of the cover material may be limiting factors here. As a consequence of the latter, it may be predicted that carbon dioxide and methane are always present within a

fermenting refuse mass. Hansson[156] made a literature review of the effects of these two gases on methanogenic fermentations and concluded that, with the exception of methanogenesis from H_2/CO_2, carbon dioxide exerted inhibitory effects on methanogens. Unfortunately, no reports regarding inhibition by methane were found, and the degrees of inhibition mediated by carbon dioxide at different pressures were not known.

Kasali[33] used sealed bottles, which contained pulverized refuse of 55% (w/w) moisture content, to examine the effects of carbon dioxide and methane on refuse methanogenesis and acidogenesis at 30°C. In all, four gases were used: OFN (control), CO_2, CH_4, and CH_4/CO_2 (60:40). Duplicate samples from each treatment were then incubated either at atmospheric pressure or under a head-space pressure of 0.6 bar (8.5 psi), for a period of 27 d. At this point the samples were assayed for total volumes of methane evolved and carboxylic acids.

The presence of carbon dioxide alone was found to have effected a 98% reduction in the volume of methane evolved compared with the OFN control, thus agreeing with the results of an earlier study.[157] In the presence of carbon dioxide, decreased concentrations of acetate were also apparent together with increased concentrations of butyrate and caproate. This apparent inhibition of acetogenesis was also reported by Hansson,[156] who recorded slight retardation of acetogenesis from butyrate but total inhibition from propionate in the presence of high concentrations of carbon dioxide. The increased concentrations of butyrate and, more particularly, caproate could be explained by the theory of interspecies hydrogen transfer,[57] whereby under conditions of inhibited methanogenic activity, these reduced acids act as hydrogen sinks, and their degradation is inhibited by high partial pressures of hydrogen.

Although the results of Kasali[33] suggested that methane generation from H_2/CO_2 in refuse was inhibited by high concentrations of carbon dioxide, these findings contrasted with those of Hansson and Molin,[153] who found no inhibition. It must be noted, however, that in the latter study the inoculum used was obtained from a sewage sludge digester and the substrate examined was glucose. In addition, the hydrogen partial pressure was regulated by interaction between the methanogens and sulfate-reducing bacteria.

The mechanisms by which carbon dioxide inhibits methanogenesis are not yet known, although it has been speculated[156] that the inhibition may be due to the raising of the redox potential. A second possibility is that carbon dioxide dissolves in the cell membranes of methanogens and impairs membrane function by increasing its fluidity. In either of these eventualities, then, both hydrogen- and acetate-utilizing methanogens would have been inhibited. In the study of Kasali[33] the presence of methane supplementations resulted in fermentation balance changes such that elevated concentrations of acetate, propionate, *iso*butyrate, butyrate, valerate, and caproate were recorded. The one exception was *iso*valerate, where a slightly reduced concentration was detected. Although, under the conditions of this experiment acetogenesis was not inhibited, it is possible that reduced methanogenesis may have resulted.[33]

In the presence of CH_4/CO_2 (60:40) elevated concentrations of acetate, *iso*butyrate, butyrate and caproate were again reported, but not propionate, *iso*valerate, and valerate. By increasing the headspace gas pressures by an approximate factor of two, fermentation balance changes were once more apparent. In particular, methanogenesis in both the OFN- and CO_2-treated samples approximately doubled. Although an explanation for this was not readily apparent, it is possible that the elevated pressures increased the phase transfer of substrates to the methanogens.[33] Despite this stimulation, however, the CO_2-supplemented samples still exhibited a 95% inhibition of methanogenesis, in conjunction with increased concentrations of butyrate, valerate, and caproate, but not acetate, compared with the OFN-treated controls. From these results Kasali[33] speculated that the elevated pressures had only affected the reaction rates, with the actual effects of the gases on refuse metabolism unchanged. Support for this possibility was found in the concentrations of acetate which were lower than in the corresponding ambient pressure treatments, possibly due to increased methanogenic activity.

If it is accepted that high partial pressures of carbon dioxide can inhibit methanogenesis in

refuse, then the carbon dioxide "blooms", which were assumed by Farquhar and Rovers[12] to occur typically in landfill, could exert adverse effects on methanogenesis. Further evidence for this was gained from the study of deWalle and Chian,[109] who were unable to establish methanogenesis in refuse samples which developed such "blooms". Similarly, Rovers and Farquhar[103] observed that in a refuse cell where the carbon dioxide concentration reached 90% by volume, only 2% by volume methane was found after an incubation period in excess of 5 months.

E. SITE STRATEGIES

Despite the number of studies made, small-scale laboratory experiments do not appear to simulate accurately the *in situ* situation.[3] However, from these studies it may be speculated that control of gas production, by manipulation of a single site variable, may result in additional operation constraints and, in addition, mediate uncontrolled changes in other factors.[159] Despite the claim by Rees[77] that the landfill fermentation can be controlled and directed by judicious manipulation of water content, thermal regime, and refuse density, so that refuse carbon compounds may be wholly converted to methane and carbon dioxide, this statement appears to be extremely speculative, particularly when one considers the significant lignin content of refuse.

Landfill site practices, which must not interfere with the day-to-day running of the site, to promote methanogenesis within a refuse mass have been described by Rees[77,160] and Stegmann,[161] In the strategy developed by Rees[160] the suggestion was made that a first lift of low density (0.35 ton/m^3) refuse, diluted with material such as wood, paper, pulverized or aerobically stabilized refuse, should be placed at the base of the fill and allowed to decompose aerobically to effect both a temperature increase and the generation of water. Subsequently, controlled water additions should be made to a discrete site area to the base of the fill via a central well and allowed to rise at a rate of between 1 and 2 m/year, thus maintaining the acetogenic and methanogenic phases in balance and also preventing excessive cooling. Rees[77] speculated that high rates of gas production would preclude the diffusion of air into the refuse mass with the cover material an important factor here. The suggestion was also made[105] that in temperate climates an insulating layer of refuse of approximately 4-m depth should be present above the reactive zone, for which the start-up could be promoted by the addition of anaerobic digester sludge, to minimize heat loss to the atmosphere.

The site operation advocated by Stegmann[161] essentially utilized the same microbiological principles as that of Rees.[160] An initial noncompacted aerobic layer was again advocated for a period of between 6 and 9 months. Following this, the suggestion was made that the refuse should be compacted in low layers over large areas and supplemented with recycled leachate. The major difference from the Rees[160] strategy was the building of the landfill as a mound with a sealed base.

For both of these strategies, control of the site water balance[115] is a critical factor to obviate abstraction difficulties which may result through partial flooding of extraction wells[3] due to, for example, the presence of high water tables.

F. ALTERNATIVE GAS GENERATION STRATEGIES

As an alternative to landfill gas generation, anaerobic digestion of refuse or landfill leachate may be considered. Before biomethanation of refuse, which is only possible in the presence of a high putrescible content,[11] pretreatment may be required to reduce the particle size and separate the organic fraction.[162] Naveau[163] examined various pretreatment options and concluded that crushing with a ball mill at elevated temperature was the most effective with respect to increased biogas yield. As an alternative to this, an initial composting step or enzyme pretreatment was advocated. Earlier, Ghosh and Klass[164] described a strategy which involved the coarse shredding

and air separation of the organic fraction prior to fiberization to a product with a median size of 0.6 mm and a moisture content of 6%. The material was then mixed with sewage sludge at a ratio of 80:20. Supplementation with liquid manure or sewage sludge to maintain the C:N:P ratio around 100:5:1 has also been advocated by many workers.[96,97,125,144,163,165-170] Finally, thermochemical pretreatment may be made after sewage sludge addition.[171] Although prior to 1985 the only full-scale operational plant was located in Sao Paolo, many laboratory and pilot-scale reactors have been described[11,97,125,144,148,162-164,166-169,172-177] in which the yields change (80 to 320 m^3/t organic matter)[163] according to the digester configuration. Both batch and continuous fermentation systems have been described and have included unstirred and completely stirred tank reactors (CSTR)[148] and plug flow systems. In addition to these single-stage systems, two-stage and two-phase bioreactors have been described. A two-phase digestion process was first described by Ghosh et al.[178] In this treament, fiberized refuse was digested in the presence of sewage sludge. Later, Augenstein et al.[173] proposed a two-phase system with recycle in which a packed bed reactor was linked with a nonbiological activated carbon system as the second phase. With the development of the UASB (upflow anaerobic sludge blanket), however, the activated carbon system was replaced by an upflow reactor.[174]

Pauss et al.[148] compared the biomethanation of refuse in a two-step process with the, often unreliable, CSTR. In all, the study was initiated with four objectives:

1. To examine the unreliability of biomethanation in a CSTR and the factors which cause it
2. To correct unreliability by use of physicochemical additives
3. To develop a more efficient process
4. To examine the feasibility of refuse biomethanation in the presence of septic tank residues

From the results of this study it was concluded that the content of refuse is particularly important since optimum biomethanation was only apparent in the presence of 16 g $CaCO_3$ per kilogram total solids. With refuse of low alkaline content it was shown that Na_2CO_3 supplementation stabilized the process. A second key component was found to be the cellulose/hemicellulose which necessitated a minimum COD refuse content of approximately 40% both to minimize the lag period and to effect high methane production in batch culture. By use of a two-step process (percolator reactor plus upflow digester), however, higher loading rates (sevenfold) could be accomodated, and these resulted in concomitant higher methane production rates (fivefold) compared with the CSTR. In a second two-stage reactor (percolation reactor plus fluidized bed digester) improved performance, compared with the CSTR, was again recorded. Finally, biomethanation of domestic refuse in the presence of septic tank residue proved to be more reliable than biomethanation of refuse alone.

Later, Naveau et al.[176] reported the development of three processes:

1. A completely-mixed water diluted process
2. A semidry process
3. A "dry" process

The final, "dry", process may be operated on a semicontinuous or continuous basis. In France, for example, a semicontinuous process for the dry fermentation of a precompost (shredded refuse after a short aerobic decomposition stage) has been investigated.[177] A similar process has been developed in Belgium where yields of 60 m^3/t refuse and 90 m^3/t of precompost have been obtained with bioreactor retention times of 2 and 3 weeks, respectively.

Whichever combination of bioreactor configuration, treatment process, and operation strategy is adopted, however, consideration should be given to the potential problem of sludge dewatering.

Unfortunately, the costs of this alternative energy recovery process are often more expensive than those associated with gas abstraction from landfilled refuse. In addition, the actual volumes of refuse involved could prove to be problematic.

To maximize gas recovery from landfill leachate would necessitate *in situ* inhibition of refuse methanogenesis. This may be accomplished by rapid elution of the refuse mass with either water or recycled leachate, thus resulting in the production of high concentrations of reduced organic acids which, in turn, would also lower the pH to the detriment of the methanogens. By manipulation of leachate production in this way consideration could also be given to the solubilization of molecules such as lignocelluloses by promotion of acid hydrolysis, which would then reduce the current protracted stabilization periods and, thus, allow the land to be returned to positive usage more quickly. One possible problem would be the solubilization of toxic heavy metals which could prove to be troublesome in the digester and, thus, necessitate a pretreatment stage.

By use of anaerobic digesters such as upflow bioreactors and fluidized beds, the methanogenic fermentation could be controlled by loading rate adjustments and, so, match energy production with industrial demands, in terms of both quantity and time periods, and this would be reflected in the digester configuration. Since leachate quality varies with time, a series of digesters would be required, the number of which would initially mirror the size of the site but would be reduced as the leachate concentration fell. This strategy would have the advantages that holding-tank storage would be minimized and the modular digesters could be moved from site to site as required. As an alternative, centralized digesters could serve a number of sites, although leachate transportation costs might prove prohibitive.

G. GAS ABSTRACTION, TREATMENT, AND USES

Over the last decade interest in gas recovery from landfill has increased considerably, with the U.S. leading the way with 81 facilities (>80% of which are owned by private sector companies) either on line or in the planning stage by 1984.[180] The European community has not been slow to respond to this challenge, however, since the two sites in operation in 1980 rose to at least 36 in 1983.[181] In the U.K. alone it has been estimated that there are at least 669 landfills which are capable of producing enough gas to generate useful amounts of power. Landfill gas abstraction is now truly global, with recovery practiced or planned in countries such as Brazil, Canada, Switzerland, and Japan.

According to Stearns,[15] gas recovery in the U.S. has been practiced on sites which vary in size from 38 to 1214 acres (average 160), although Bogardus[7] later reported an extended range of 15 to 1500 acres with an average site size of 169 acres. In the U.K. the sites are somewhat smaller with the largest (Aveley) 25 ha and the smallest (Bilham Grange Farm) only 4 ha. Characteristically, refuse depths in these sites have been between 20 and 300 ft with an average of 100 ft.[15] Feasibility of commercial gas extraction is often based on the satisfaction of specific site criteria:[7] 1 to 2 million t of in-place refuse; an average refuse depth of 40 ft; an active fill area of 40 acres; a refuse intake of 400 t/d; the landfill either recently closed or, preferably, still active; and a market for the gas in close proximity.

1. Abstraction

One method commonly used for recovering landfill gas is pumping from recovery wells which are linked to vertical or horizontal perforated pipes.[159,182] Abstraction is, however, often preceded by indirect determination of gas production rates by methods such as those described by deWalle and Chian[109] and Rees[105] rather than the much more valid radiotracer technique.[183] The development of an effective gas abstraction system necessitates experimental evaluation of a number of factors including:

1. Selection of a withdrawal rate that can realize gases with maximum (and approximately constant) heating values

2. Establishment of adequate pressure gradients to assure scavenging of landfill gases without interference with adjacent wells
3. Optimization of the energy requirement for gas withdrawal
4. Determination of the numbers and locations of gas wells

In order to achieve these goals, a test well and supporting monitoring wells must be drilled and a series of static and short-run tests made to evaluate landfill pressure profiles (static and dynamic), gas composition and heating values, and constancy of withdrawal rates.[5]

Typically, vertical wells are sunk into the refuse by boring or punching. Perforated pipes are then placed centrally within these and each annulus filled with granular material such as gravel, crushed stone, or broken brick. The upper portion of each pipe is unperforated, and here the annulus is filled with a sealing material such as concrete, bentonite, or polyurethane foam. The wells, usually sited between 100 and 150 m apart; are then connected by horizontal pipes which are usually of polyethylene, or polyvinyl chloride (PVC) material.[159,184] Alternatively, car tires may be used.[159] Pumps[2,161,185] may then be applied to establish a pressure gradient within the landfill and thus facilitate gas flow into the wells which are fitted with control valves. As an alternative, blowers[161] may be applied to increase the recovery efficiency. At this stage care must be taken to ensure that the negative pressures created do not effect atmospheric gas penetration of the soil cover.[96] In this eventuality aerobic environments would be created which not only would be detrimental to methanogenesis, but also would result in the generation of concentrations of carbon dioxide which would reduce the calorific quality of the abstracted gas. To minimize these potential problems Vestraere et al.[96] suggested a maximum drain overpressure of <0.5 mbar.

As an alternative to the vertical wells, perforated pipes may be placed horizontally and connected in a grid-like network. This type of abstraction, however, which is often used in shallow sites, necessitates that the landfills be built up to the finished level, with due regard to settlement, as quickly as possible. The area of working is, therefore, restricted which, in turn, can make the laying of the wells more difficult. A third alternative for gas collection is polyethylene dome coverage, of a specific site area, which was evaluated by Moss[illegible] in refuse lysimeter studies. For site operation, however, sealing problems exist. In addition, the costs are high, although, as yet, no comparable figures are available for the three different collection methods.

The actual choice of gas recovery strategy is, however, often made on the basis of whether refuse emplacement is still in progress.[159]

2. Treatment and Storage

Once recovered, landfill gas may be subjected to treatment[illegible] prior to use. Gas clearing techniques include dehydration, to remove condensate and reduce corrosion and adsorption, liquefaction and adsorption, to remove carbon dioxide and hydrogen sulfide, and particulate removal. A number of gas purification processes are commercially available and have had long use in the petrochemical industry.

Although landfill gas production could be relatively constant with little short-term change, utilization could, nevertheless, be subject to changes. Thus, consideration should be given to the following:

1. If gas production exceeds demand, intermediate gas storage is not required, although a considerable loss of gas may be anticipated.
2. If gas production is lower than peak demand, gas storage may be necessitated to optimize gas usage.

In principle, only high-grade gas mixtures, with minimal oxygen contents, should be stored. Unfortunately, compression containers are unsuitable for storing landfill gas due to the fact that

the critical temperature of methane (Tk = –82.5°C) is too low for liquefaction at room temperature. Thus, suitable compression containers would require endurance pressures >200 bar.

3. Gas Uses

Once the feasibility if gas abstraction is established, consideration should be given to methods of effective exploitation which may include:

1. Direct use of low Btu gas with minimal cleaning (a) injection into existing natural gas transmission lines (b) delivery to adjacent interruptable gas consumer (c) on-site generation of electrical power
2. On-site cleaning to high Btu gas for direct pipeline use (≙ 100% methane)
3. On-site conversion of methane to liquified natural gas
4. On-site conversion of methane to methanol

Landfill gas, with a low Btu of 400 to 700 per standard cubic foot,[185] has been used as a low-grade fuel, for example, to fire brick, and cement kilns, raise steam, and heat greenhouses.[7,14–16,18,182,186,191,192] Since minimal cleaning is required, this represents a low capital investment. Alternatively, the gas may be injected directly into a natural gas transmission line after dehydration and possible removal of toxic components to obviate potential corrosion problems. Direct gas use for electric power generation[7,18,161,190,193] has been demonstrated at, for example, the Sheldon-Arleta landfill, Los Angeles, where a substantial recovery of net energy was made. Unfortunately, in many cases, the conversion efficiency may be as low as 30%.[186]

Although purification to upgrade the gas, to give a Btu of 900 to 1000 per standard cubic foot may require substantial investment in capital equipment, the gas may then be injected directly into pipelines.[7,15] Alternatively, the gas may then be liquified (300 lb psi)[186] for fuel,[7,14,18] although since the costs involved are relatively high, this technology may be limited to sites with high gas deliverability. Finally, consideration may be given to conversion to products such as methanol and chemical feedstock,[7] hydrocarbon fuel replacement, and coal replacement, of which the latter two have conversion efficiencies of 95 and 85%, respectively.[186]

Whatever the final use, however, the benefits of the energy produced may be maximized by usage at the landfill, although where industries are established to take advantage of this, then due consideration should be given to possible problems, such as gas seepage and land settlement.[191,194]

REFERENCES

1. **deWalle, F. B., Chian, E. S. K., and Hammerberg, E.**, Gas production from solid waste in landfills, *J. Environ. Eng. Div.*, EE3, 415, 1978.
2. **Parker, A.**, Landfill gas problems — case histories, in *Landfill Gas Symp. Papers*, Harwell, 1981, pap. 3.
3. **Stearns, R. P. and Wright, T. D.**, Landfill gas recovery at the Ascon disposal site — a case study, in *Fuels from Biomass and Wastes*, Klass, D. L. and Emert, G. H., Eds., Ann Arbor Science Publishers, Ann Arbor, MI, 1981, 199.
4. **Young, P. J. and Parker, A.**, The identification and possible environmental impact of trace gases and vapours in landfill gas, *Waste Manage. Res.*, 1, 213, 1983.
5. **EMCON Associates**, *Methane Generation and Recovery from Landfills*, Ann Arbor Science Publishers, Ann Arbor, MI, 1980.
6. **Lucas, J. L. and White, G. C.**, Design and instrumentation of a semi-permeable attenuation blanket beneath a domestic waste landfill, in *Reclamation 83 Papers*, Industrial Seminars Inc., Tunbridge Wells, England, 1983, 299.

7. **Bogardus, E. R.**, Should you recover landfill gas?, *BioCycle*, 25, 48, 984.
8. **Bishop, W. D., Carter, R. C., and Ludwig, H. F.**, Gas movement in landfilled rubbish, *Public Works*, 96, 64, 1965.
9. **Baker, J. M., Peters, C. J., Perry, R., and Knight, C. P. V.**, Odour problems associated with solid waste disposal, *Public Health Eng.*, 12, 115, 1984.
10. **Doyle, A. A.**, New landfill breaks new ground, *Public Works*, 116(11), 59, 1985.
11. **Parker, C. and Roberts, T.**, *Energy from Waste: An Evaluation of Conversion Technologies*, Elsevier Applied Science Publishers, London, 1985.
12. **Farquhar, G. J. and Rovers, F. A.**, Gas production during refuse decomposition, *Water Air Soil Pollut.*, 2, 483, 1973.
13. **Parry, G. D. R.**, Afteruse of landfill sites, in *Landfill Gas Symp. Papers*, Harwell, 1981, pap. 8.
14. **Marchant, A. J.**, Practical aspects of landfill gas — a local authority view, in *Landfill Gas Symp. Papers*, Harwell, 1981, pap. 7.
15. **Stearns, R. P.**, Landfill methane: 23 sites are developing recovery systems, *Solid Waste Manage. R.R.J.*, 6, 56, 1980.
16. **Cheyney, A. C. and Moss, H. D. T.**, Landfill gas as an energy source, in *Landfill Gas Symp. Papers*, Harwell, 1981, pap. 9.
17. **Mancinelli, R. L., Shulls, W. A., and McKay, C. P.**, Methanol-oxidizing bacteria used as an index of soil methane content, *Appl. Environ. Microbiol.*, 42, 70, 1981.
18. **Knop, R.**, Use of landfill gas as an automotive fuel, in *Anaerobic Digestion and Carbohydrate Hydrolysis of Waste*, Ferrero, G. L., Ferranti, M. P., and Naveau, H., Eds., Elsevier Applied Science Publishers, London, 1984, 405.
19. **Bohn, H. L.**, Soil and compost filters of malodorant gases, *J. Air Pollut. Control Assoc.*, 25, 953, 1975.
20. **Roberts, R. D.**, personal communication.
21. **Marchant, A. J.**, The sweet smell of success? Landfill gas its problems and uses, *Wastes Manage.*, 72, 236, 1982.
22. **Ehhalt, D. H.**, Atmospheric circulation of methane, *Naturwissenschaften*, 66, 307, 1979.
23. **Forster, C. F.**, *Biotechnology and Wastewater Treatment*, *Cambridge Studies in Biotechnology* 2, Cambridge University Press, London, 1985.
24. **Jeris, J. S. and McCarty, P. L.**, The biochemistry of methane fermentation using C^{14} tracers, *J. Water Pollut. Control Fed.*, 37, 178, 1965.
25. **Mah, R. A., Ward, D. M., Baresi, L., and Glass, T. L.**, Biogenesis of methane, *Annu. Rev. Microbiol.*, 31, 309, 1977.
26. **Wolfe, R. S.**, Biochemistry of methanogenesis, *Experientia*, 38, 198, 1982.
27. **Schoberth, S. M.**, The microbiology of anaerobic digestion, in *Biomethane: Production and Utilisation*, Barnes, R. H. Fox, M. F., and Picken, D. J., Eds., Turret-Wheatland, Rickmansworth, U.K., 1982, 61.
28. **Oremland, R. S., Marsh, L. M., and Polcin, S.**, Methane production and simultaneous sulphate reduction in anoxic, saltmarsh sediments, *Nature (London)*, 296, 143, 1982.
29. **Oremland, R. S. and Polcin, S.**, Methanogenesis and sulphate reduction: competitive and non-competitive substrates for estuarine sediments, *Appl. Environ. Microbiol.*, 44, 1270, 1982.
30. **King, M. G.**, Metabolism of trimethylamine, choline and glycine betaine by sulphate-reducing and methanogenic bacteria in marine sediments, *Appl. Environ. Microbiol.*, 48, 719, 1984.
31. **Ferguson, J. T. and Mah, A. M.**, Effect of H_2-CO_2 on methanogenesis from acetate or methanol in *Methanosarcina* spp., *Appl. Environ. Microbiol.*, 46, 348, 1983.
32. **Senior, E. and Balba, M. T. M.**, unpublished observations.
33. **Kasali, G. B.**, Optimization and Control of Methanogenesis in Refuse Fractions, Ph.D. thesis, University of Strathclyde, Glasgow, U.K., 1986.
34. **Hoeks, J. and Borst, R. J.**, Anaerobic digestion of free volatile fatty acids in soils below waste tips, *Water Air Soil Pollut.*, 17, 165, 1982.
35. **Pfennig, N. and Widdel, F.**, The bacteria of the sulphur cycle, *Philos. Trans. R. Soc. London B.*, 298, 43[illegible], 1982.
36. **Schink, B. and Zeikus, J. G.**, Microbial ecology of pectin decomposition in anoxic lake sediments, *Arch. Microbiol.*, 128, 393, 1982.
37. **Balba, M. T. M., Clark, N. A., and Evans, W. C.**, The methanogenic fermentation of plant phenolics, *Biochem. Soc. Trans.*, 7, 115, 1979.
38. **McInerney, M. J., Bryant, M. P., and Pfennig, N.**, Anaerobic bacterium that degrades fatty acids in syntrophic association with methanogens, *Arch. Microbiol.*, 122, 129, 1979.
39. **Fathepure, B. Z.**, Isolation and characterisation of an acetoclastic methanogen from a biogas digester, *FEMS Microbiol. Lett.*, 19, 151, 1983.
40. **Balch, W. E., Schobert, D., Tanner, R. S., and Wolfe, R. S.**, *Acetobacterium*, a new genus of hydrogen oxidising carbon dioxide reducing, anaerobic bacteria, *Int. J. Syst. Bacteriol.*, 27, 355, 1977.

41. **Braun, M. and Gottschalk, G.,** *Acetobacterium wieringae* sp. nov., a new species producing acetic acid from molecular hydrogen and carbon dioxide, *Zentralbl. Bakteriol. Parasitenkd. Infektiorskr. Hyg. Abt. 1: Orig. Reihe*, C 3, 368, 1982.
42. **Jones, J. G. and Simon, B. M.,** Interaction of acetogens and methanogens in anaerobic freshwater sediments, *Appl. Environ. Microbiol.*, 49, 944, 1985.
43. **Coutts, D. A. P.,** Terminal Anaerobic Interactions in a Microbial Association Isolated from Landfill, Ph.D. thesis, University of Strathclyde, Glasgow, U.K., 1986.
44. **Coutts, D. A. P., Senior, E., and Balba, M. T. M.,** Multi-stage chemostat investigation of interspecies interactions in a hexanoate-catabolising microbial association isolated from anoxic landfill, *J. Appl. Bacteriol.*, 62, 251, 1987.
45. **Rees, J. F.,** The fate of carbon compounds in the landfill disposal of organic matter, *J. Chem. Technol. Biotechnol.*, 30, 161, 1980.
46. **Balch, W. E., Fox, G. E., Magrum, L. J., Woese, C. R., and Wolfe, R. S.,** Methanogens: a re-evaluation of a unique biological group, *Microbiol. Rev.*, 43, 260, 1979.
47. **Smith, M. R., Zinder, S. H., and Mah, R. A.,** Microbial methanogenesis from acetate, *Process Biochem.*, 15, 34, 1980.
48. **Lovely, D. R. and Ferry, J. G.,** Production and consumption of hydrogen during growth of *Methanosarcina* spp. on acetate, *Appl. Environ. Microbiol.*, 49, 247, 1985.
49. **Huser, B. A., Wuhrmann, K., and Zehnder, A. J. B.,** *Methanothrix soehngenii* gen. nov. sp. nov., a new acetotrophic non-hydrogen-oxidizing methane bacterium, *Arch. Microbiol.*, 132, 1, 1982.
50. **Patel, G. B.,** Characterisation and nutritional properties of *Methanothrix concilii* sp. nov., a mesophilic aceticlastic methanogen, *Can. J. Microbiol.*, 30, 1383, 1984.
51. **Schink, B.,** Microbial degradation of pectin in plants and aquatic environments, in *Current Perspectives in Microbial Ecology*, Klug, M. J. and Reddy, C. A., Eds., American Society of Microbiology, Washington, D.C., 1984, 580.
52. **Neill, A. R., Grime, D. W., and Dawson, R. M. C.,** Conversion of choline methyl groups through trimethylamine into methane in the rumen, *Biochem. J.*, 170, 529, 1978.
53. **King, M. G., Klug, J. M., and Lovley, D. R.,** Metabolism of acetate, methanol and methylated amines in intertidal sediments of Lowes Cove, Maine, *Appl. Environ. Microbiol.*, 45, 1848, 1983.
54. **Walther, R., Fahlbusch, K., Sievert, R., and Gottschalk, G.,** Formation of trideutromethane from deuterated trimethylamine or methaylamine by *Methanosarcina barkeri*, *J. Bacteriol.*, 148, 371, 1981.
55. **Harmsen, J.,** Identification of organic compounds in leachate from a waste tip, *Water Res.*, 17, 699, 1983.
56. **Zeikus, J G.,** Metabolism of one-carbon compounds by chemotrophic anaerobes, *Adv. Microb. Physiol.*, 24, 215, 1983.
57. **Zeikus, J. G.,** The biology of methanogenic bacteria, *Bacteriol. Rev.*, 41, 514, 1977.
58. **Zehnder, A. J. B. and Brock, T. D.,** Methane formation and methane oxidation by methanogenic bacteria, *J. Bacteriol.*, 137, 420, 1979.
59. **Wuhrmann, K.,** Ecology of methanogenic systems in nature, *Experientia*, 38, 193, 1982.
60. **Wolfe, R. S.,** Microbial biochemistry of methane — a study in contrast, in *International Review of Biochemistry, Microbial Biochemistry*, Volume 21, Quayle, J. R., Ed., University Park Press, Baltimore, 1979, chap. 7.
61. **Taylor, C. D. and Wolfe, R. S.,** Structure and methylation of coenzyme M ($HSCH_2CH_2SO_3$), *J. Biol. Chem.*, 249, 4879, 1974.
62. **Eirich, L. D., Vogels, G. D., and Wolfe, R. S.,** Proposed structure of co-enzyme F_{420} from *Methanobacterium*, *Biochemistry*, 17, 4583, 1978.
63. **Gunsalus, R. P., and Wolfe, R. S.,** Chromophoric factors F_{342} and F_{420} of *Methanobacterium thermoautotrophicum*, *FEMS Microbiol. Lett.*, 3, 191, 1978.
64. **Keltjens, J. T. M.,** Conezymes of Methanogenesis, Ph.D. thesis, University of Nijmegen, The Netherlands.
65. **Cheesman, P. A., Toms-Wood, T., and Wolfe, R. S.,** Isolation and properties of fluorescent compound factor 420, from *Methanobacterium* strain M.O.H., *J Bacteriol.*, 112, 527, 1972.
66. **Taylor, C. D., McBride, B. C., Wolfe, R. S., and Bryant, M. P.,** Coenzyme M, essential for the growth of a rumen strain of *Methanobacterium ruminantium*, *J. Bacteriol.*, 120, 974, 1974.
67. **Dubach, A. C. and Bachofen, R.,** Methanogens: a short taxonomic overview, *Experientia*, 41, 441, 1985.
68. **Woese, C. R.,** Archaebacteria and cellular origins: an overview, *Zentralbl. Bakteriol. Parasitenkd. Infektionskr. Hyg. Abt. I:Orig.*, C3, 1, 1982.
69. **Emery, R. S., Smith C. K., and Huffmann, C. F.,** Utilisation of inorganic sulfate by rumen microorganisms. I. Incorporation of inorganic sulfate into amino acids, *Appl Microbiol.*, 5, 360, 1957.
70. **Emery, R. S., Smith, C. K., and Fai To, L.,** Utilisation of inorganic sulfate by rumen microorganisms. II. The ability of single strains of rumen bacteria to utilise inorganic sulfate, *Appl. Microbiol.*, 5, 563, 1957.
71. **Valentine, R. C.,** Bacterial ferredoxin, *Bacteriol. Rev.*, 28, 497, 1964.
72. **McBride, B. C. and Wolfe, R. S.,** A new coenzyme of methyl transfer, coenzyme M, *Biochemistry*, 10, 2317, 1971.

73. **Malkin, R. and Rabinowitz, J. C.,** Non-heme iron electron-transfer proteins, *Annu. Rev. Biochem.*, 36, 113, 1967.
74. **Khan, A. W. and Trottier, T. M.,** Effect of sulphur-containing compounds on anaerobic degradation of cellulose to methane by mixed cultures obtained from sewage sludge, *Appl. Environ. Microbiol.*, 35, 1027, 1978.
75. **Nagase, M. and Matsuo, T.,** Interactions between amino acid degrading bacteria and methanogenic bacteria in anaerobic digestion, *Biotechnol. Bioeng.*, 24, 2227, 1982.
76. **Robinson, H. D. and Maris, P. J.,** Leachate from Domestic Waste: Generation, Composition and Treatment, Tech. Rep. U.K. Water Research Centre, Stevenage, 1979, 108.
77. **Rees, J. F.,** Optimisation of methane production and refuse decomposition in landfill by temperature control, *J. Chem. Technol. Biotechnol.*, 30, 458, 1980.
78. **Forster, C. F. and Senior, E.,** Solid waste, in *Environmental Biotechnology*, Forster, C. F. and Wase, D. A. J., Eds., Ellis Horwood, Chichester, 1987, 176
79. **Gottschalk, G.,** Bacterial fermentation, in *Bacterial Metabolism*, Springer-Verlag, Basel, 1978, chap. 8.
80. **Henze, M. and Harremoes, P.,** Anaerobic treatment of wastewater in fixed film reactors — a literature review, *Water Sci. Technol.*, 15 (8/9), 1, 1983.
81. **Speece, R. E. and Parkin, G. F.,** The response of methane bacteria to toxicity, in *Proc. 3rd Int. Symp. Anaerobic Digestion*, 1983, 23.
82. **Ehrig, H. J.,** Quality and quantity of sanitary landfill leachate, *Waste Manage. Res.*, 1, 53, 1983.
83. **Ferry, J. G. and Wolfe, R. S.,** Anaerobic degradation of benzoate to methane by a microbial consortium, *Arch. Microbiol.*, 107, 33, 1976.
84. **Mountfort, D. O. and Bryant, M. P.,** Isolation and characterisation of anaerobic syntrophic benzoate degrading bacterium from sewage sludge, *Arch. Microbiol.*, 133, 249, 1982.
85. **Cappenberg, Th. E.,** Interrelations between sulfate reducing and methane producing bacteria in bottom deposits of a freshwater lake. II. Inhibition experiments, *Antonie van Leeuwenhoek J. Microbiol. Serol.*, 40, 297, 1974.
86. **Cappenberg, Th. E.,** A study of mixed continuous cultures of sulphate-reducing and methane-producing bacteria, *Microb. Ecol.*, 2, 60, 1975.
87. **Laanbroek, H. J. and Veldkamp, H.,** Microbiol interactions in sediment communities, *Philos. Trans. R. Soc. London Ser. B*, 297, 533, 1982.
88. **Finney, C. D. and Evans, R. S.,** Anaerobic digestion: the rate-limiting process and the nature of inhibition, *Science*, 190, 1088, 1975.
89. **Devol, A. H. and Ahmed, S. I.,** Are high rates of sulphate reduction associated with anaerobic oxidation of methane?, *Nature (London)*, 291, 407, 1981.
90. **Ham, R. K.,** Predicting gas generation from landfills, *Waste Age*, 11, 50, 1979.
91. **White, L. P. and Plaskett, L. G.,** *Biomass as Fuel*, Academic Press, London, 1981.
92. **Boyle, W. C.,** Energy recovery from sanitary landfills — a review, in *Microbial Energy Conversion*, Schlegel, H. G. and Barnea, J., Eds., Pergamon Press, Oxford, 1977, 119.
93. **Pauss, A., Nyns, E. J., and Naveau, H.,** Production of methane by anaerobic digestion of domestic refuse, in *Anaerobic Digestion and Carbohydrate Hydrolysis of Waste*, Ferrero, G. L., Ferranti, M. P., and Naveau, H., Eds., Elsevier Applied Science Publishers, London, 1984, 209.
94. **Marriott, J.,** Some practical aspects of control of leachate from landfill sites, *Solid Wastes*, 71, 51[illegible], 1981.
95. **Buivid, M. G., Wise, D. L., Blanchet, M. J., Remedios, E. C., Jenkins, B. M., Boyd, W. F., and Pacey, J. G.,** Fuel gas enhancement by controlled landfilling of municipal solid waste, *Resour. Conserv.*, 6, 3, 1981.
96. **Verstraete, W., Valcke, D., Vaes, H., and Popelier, F.,** Production of methane by anaerobic digestion of domestic refuse and compost, in Proc. Int. Symp. Anaerobic Digestion and Carbohydrate Hydrolysis of Waste, Luxembourg, 1984, 27.
97. **Augenstein, D. C., Wise, D. L., Wentworth, R. L., and Cooney, C. L.,** Fuel gas recovery from controlled landfilling of municipal wastes, *Resour. Recov. Conserv.*, 2, 103, 1976.
98. **Leckie, O. J., Pacey, J. G., and Halvadakis, C.,** Landfill management with moisture control, *J. Env. Eng. Div. Am. Soc. Civ. Eng.*, 105, 337, 1979.
99. **Straub, W. B. and Lynch, D. R.,** Models of landfill leaching: moisture flow and inorganic strength, *J. Env. Eng. Div. Am. Soc. Civ. Eng.*, 108, 231, 1982.
100. **Pirt, S.J.,** *Principles of Microbe and Cell Cultivation*, Blackwell Scientific, Oxford, 1975
101. **Dobson, A. L.,** Microbial Decomposition Investigations in Sanitary Landfills, Ph.D. thesis, University of West Virginia, Springfield, 1964.
102. **Merz, R. C., and Stone, R.,** Quantitative study of the gas produced by decomposing refuse, *Public Works*, 86, 1968.
103. **Rovers, F. A. and Farquhar, G. J.,** Infiltration and landfill behaviour, *J. Environ. Eng. Div. Am. Soc. Civ. Eng.*, 99, 671, 1973.
104. **Klink, F. R. and Ham, R. K.,** Effects of moisture movement on methane production in municipal waste landfill samples, *Resour. Recov. Conserv.*, 8, 29, 1982.

Rees, J. F., Major factors affecting methane production in landfills, in *Landfill Gas Symp. Papers*, Harwell, 1981, pap. 2.

Rees, J. F. and Grainger, J. M., Rubbish dump or fermenter? Prospects for the control of refuse fermentation to methane in landfills, *Process Biochem.* 17, 41, 1982.

Marriott, J., Some practical aspects of control of leachate from landfill sites, *Solid Wastes*, 71, 513, 1981.

Findikakis, A. N. and Leckie, J. O., Numerical simulation of gas flow in sanitary landfills, *J. Environ. Eng. Div. Am. Soc. Civ. Eng.*, 105, 927, 1979.

deWalle, F. B. and Chian, E. S. K., Energy recovery from landfilled solid waste, *Biotechnol., Bioeng. Symp.*, 9, 317, 1979.

Ghosh, S., Solid-phase digestion of low-moisture feeds, *Biotechnol. Bioeng. Symp.*, 14, 365, 1984.

Baronofsky, J. J., Schreurs, W. J. A., and Kashket, E. R., Uncoupling of acetic acid limits growth of and acetogenesis by *Clostridium thermoaceticum*, *Appl. Environ. Microbiol.*, 48, 1134, 1984.

Wang, G. and Wang, D. I. C., Elucidation of growth inhibition and acetic acid production by *Clostridium thermoaceticum*, *Appl. Environ. Microbiol.*, 47, 294, 1984.

Ramaswamy, J. N., Nutritional Effects on Acid and Gas Production in Sanitary Landfills, Ph.D. thesis, University of West Virginia, Springfield, 1970.

Hartz, K. E., Methanogenesis in Landfills, Ph.D. thesis, University of Wisconsin, LaCrosse, 1980.

Campbell, D. J. V., Understanding water balance in landfill sites, *Wastes Manage.*, 73, 594, 1983.

Jackson, A. G. and Streng, D. R., Gas and leachate generation in various solid waste environments, in *Gas and Leachate from Landfill: Formation, Collection and Treatment*, Genetelli, E. J., and Cirello, J., Eds., EPA-600/9-76-004, U.S. Environmental Protection Agency, Washington, D.C., 1976, 83.

Franklin, A. G., Chakraverty, C., and Quon, J. E., Time-Settlement Behavior of Processed Refuse, Final Rep. III. Anaerobic Digestion of Milled Refuse, US EPA-600-2-81-135, U.S. Environmental Protection Agency, Washington, D.C., 1981.

Hartz, K. E., Klink, R. E., and Ham, R. K., Temperature effects: methane generation from landfill samples, *J. Environ. Eng. Div. Am. Soc. Civ. Eng.*, 108 (EE4), 629, 1982.

Wigh, R. J., Landfill research at Boone County field site, U.S. National Technical Information Service, Springfield, VA, Report No. PB84-161546, 1984.

Rovers, F. A. and Farquhar, G. J., Effect of Seasons on Landfill Leachate and Gas Production, Waterloo Research Institute, Project 8083, Waterloo, Ontario, Canada, 1972.

Cooney, C. L. and Wise, D. L., Thermophilic anaerobic digestion of solid waste for fuel gas production, *Biotechnol. Bioeng.*, 17, 1119, 1975.

Pfeffer, J. T. and Khan, K. A., Microbial production of methane from municipal refuse, *Biotechnol. Bioeng.*, 18, 1179, 1976.

Zinder, S. H., Anguish, T., and Cardwell, S. C., Effects of temperature on methanogenesis in a thermophilic (58°C) anaerobic digester, *Appl. Environ. Microbiol.*, 47, 808, 1984.

Merz, R. C. and Stone, R., Special studies of a sanitary landfill, Department of Civil Engineering, University of Southern California, 1969.

Pfeffer, J. T., Temperature effects on anaerobic fermentation of domestic refuse, *Biotechnol. Bioeng.*, 16, 771, 1974.

Stuckey, D., Technology Assessment Study of Biogas in Developing Countries, Interim Rep. to the World Bank, International Reference Centre for Waste Disposal, Dubendorf, Switzerland, 1982.

Merz, R. C. and Stone, R., Special Studies of a Sanitary Landfill, US-EPA-SW-8R6-70, U.S. Environmental Protection Agency, Washington, D.C., 1968.

Holt, A. R., Stephens, M. G., and Morris, G. J., Production of solvents by *Clostridium acetobutylicum* cultures maintained at neutral pH, *Appl. Environ. Microbiol.*, 48, 1166, 1984.

Zanoni, A. E., Potential for groundwater pollution from the land disposal of solid wastes, *Crit. Rev. Environ. Control*, 3, 225, 1973.

Baedecker, M. J. and Back, W., Modern marine sediments as a natural analog to the chemically stressed environment of a landfill, *J. Hydrol.*, 43, 393, 1979.

Stumm, W. and Morgan, J. J., *Aquatic Chemistry*, John Wiley & Sons, New York, 1970.

Bookter, J. T. and Ham, R. K., Stabilisation of solid waste in landfills, *J. Environ. Eng. Div Am. Soc. Civ. Eng.*, 108(EE6), 1089, 1982.

Datta, R. and Zeikus, J. G., Modulation of acetone-butanol-ethanol fermentation by carbon monoxide and organic acids, *Appl. Environ. Microbiol.*, 49, 522, 1985.

Kell, D. B., Peck, M. W., Rodger, G., and Morris, G. J., On the permeability to weak acids and bases of the cytoplasmic membrane of *Clostridium pasteurianum*, *Biochem. Biophys. Res. Commun.*, 99, 81, 1981.

Jarrell, K. F. and Sprott, D. G., The transmembrane electrical potential and intracellular pH in methanogenic bacteria, *Can. J. Microbiol.*, 27, 720, 1981.

Gale, E. F., *The Chemical Activities of Bacteria, 3rd ed.*, University Tutorial Press, London, 1951, 144.

Jöbses, M. L. and Roels, J. A., Experience with solvent production by *Clostridium beijerinckii* in continuous culture, *Biotechnol. Bioeng.*, 25, 1187, 1983.

Roos, J. W., McLaughlin, J. K., and Papoutsakis, E. T., The effect of pH on nitrogen supply, cell lysis, and solvent production in fermentations of *Clostridum acetobutylicum*, *Biotechnol. Bioeng.*, 27, 681, 1985.

Genthner, B. R. S., Davis, C. L., and Bryant, M. P., Features of rumen and sewage sludge strains of *Eubacterium limosum*, a methanol-1 and H_2-CO_2-utilizing species, *Appl. Environ. Microbiol.*, 42, 12, 1981.

Adamse, A. D. and Velseboer, C. T. M., Features of a *Clostridium*, strain CV-AA1, an obligatory anaerobic bacterium producing acetic acid from methanol, Antonie van Leeuwenhoek, *J. Microbiol. Serol.*, 48, 305, 1982.

Laanbroek, H. J., Abee, T., and Voogd, J. L., Alcohol conversions by *Desulfobulbus propionicus* Lindhorst in the presence and absence of sulphate and hydrogen, *Arch. Microbiol.*, 133, 178, 1982.

McInerney, M. and Bryant, M. P., Basic principles of bioconversions in anaerobic digestion and methanogenesis, in *Biomass Conversion Processes for Energy and Fuels*, Sofer, S. S. and Zaborosky, O. R., Eds., Plenum Press, New York, 1981, 277.

Mao, M. C. and Pohland, F. G., Continuing Investigations on Landfill Stabilization with Leachate Recirculation, Neutralization and Sludge Seeding, Spec. Res. Rep., Department of Civil Engineering, Georgia Institute of Technology, Atlanta, 1973.

Klein, S. A., Anaerobic digestion of solid wastes, *Compost Sci.*, 13(1), 6, 1972.

Gossett, J. M., Stuckey, D. C., Owen, W. F., and McCarty, P. L., Heat treatment and anaerobic digestion of refuse, *J. Environ. Eng. Div. Am. Soc. Civ. Eng.*, 108, 437, 1982.

Mosey, F. E., Swanwick, D. J., and Hughes, A. D., Factors affecting the availability of heavy metals to inhibit anaerobic digestion, *Water Pollut. Control*, 72, 668, 1971.

de Baere, L. A., de Vocht, M., van Assche, P., and Verstraete, W., Influence of high NaCl and NH_4Cl salt levels in methanogenic associations, *Water Res.*, 18, 543, 1984.

Pauss, A., Nyns, E. J., and Naveu, H., Production of methane by anaerobic digestion of domestic refuse, in *Anaerobic Digestion and Carbohydrate Hydrolysis of Waste*, Ferrero, G. L., Ferranti, M. P., and Naveau, H., Eds., Elsevier Applied Science Publishers, London, 1984, 209.

Schlegel, H. G., Production, modification and consumption of atmospheric trace gases by microorganisms, *Tellus*, 26, 11, 1974.

Scheifinger, C. C., Linehan, B., and Wolin, M. J., H_2 production by *Selenomonas ruminantium* in the absence and presence of methanogenic bacteria, *Appl. Microbiol.*, 29, 480, 1975.

Winfrey, M. R., Nelson, D. R., Klevickis, S. C., and Zeikus, J. G., Association of hydrogen metabolism with methanogenesis in Lake Mendota sediments, *Appl. Environ. Microbiol.*, 33, 312, 1977.

Wolin, M. J., Metabolic interactions among intestinal microorganisms, *Am. J. Clin. Nutr.*, 27, 1320, 1974.

Hansson, G. and Molin, N., End-product inhibition in methane fermentations: effects of carbon dioxide and methane on methanogenic bacteria utilizing acetate, *Eur. J. Appl. Microbiol. Biotechnol.*, 15, 236, 1982.

Mountfort, D. O., Asher, R. A., Mays, E. L., and Tiedje, J. M., Carbon and electron flow in mud and sandflat intertidal sediments at Delaware Inlet, Nelson, New Zealand, *Appl. Environ. Microbiol.*, 39, 686, 1980.

Massey, M. L. and Pohland, G. F., Phase separation of anaerobic stabilisation by kinetic control, *J. Water Pollut. Control Fed.*, 50, 2205, 1978.

Hansson, G., End-product inhibition in methane fermentations, *Process Biochem.*, 17(6), 45, 1982.

Hansson, G., Effects of carbon dioxide and methane on methanogenesis, *Eur. J. Appl. Microbiol. Biotechn.* 6, 351, 1979.

Robinson, H. D. and Tiedje, J. M., Kinetics of hydrogen consumption by rumen fluid, anaerobic digestion sludge and sediment, *Appl. Environ. Microbiol.*, 44, 1374, 1982.

Mouton, C., Methane production and recovery from household waste landfill, in *Anaerobic Digestion and Carbohydrate Hydrolysis of Waste*, Ferrero, G. L., Ferranti, M. P., and Naveau, H., Eds., Elsevier Applied Science Publishers, London, 1984, 395.

Rees, J. F., Landfill management and leachate quality, *Effluent Water Treat. J.*, 22, 457, 1982.

Stegmann, R., Landfill gas problems — summary of West German experience, in *Landfill Gas Symp. Pap.*, Harwell, 1981, pap.6.

van der Vlugt, A. J. and Rulkens, W. H., Biogas production from a domestic waste fraction, in *Anaerobic Digestion and Carbohydrate Hydrolysis of Water*, Ferrero, G. L., Ferranti, M. P., and Naveau, H., Eds., Elsevier Applied Science, London, 1984, 245.

Naveau, H., Anaerobic digestion in the EEC, in *Anaerobic Digestion and Carbohydrate Hydrolysis of Waste*, Ferrero, G. L., Ferranti, M. P., and Naveau, H., Eds., Elsevier Applied Science Publishers, London, 1984, 182.

Ghosh, S. and Klass, D., The production of substitute natural gas and recyclables from municipal solid waste, in *Recycling Berlin '79*, Thome-Kozmiensky, K. J., Ed., Freitag-Verlag fur Umwelttechnik, Berlin, 1979, 759.

Diaz, L. F., Savage, G. M., and Golueke, C. G., *Resource Recovery from Municipal Solid Wastes, Volume II. Final Processing*, CRC Press, Boca Raton, FL, 1982.

Hitte, S. J., Anaerobic digestion of solid waste and sewage sludge into methane, *Compost Sci.*, 17(1), 20, 1976.

167. **Kispert, R. G., Sadek, S. E., and Wise, D. L.**, An evaluation of methane production from solid waste, *Res. Recov. Conserv.*, 1, 245, 1976.
168. **le Roux, N. W. and Wakerley, D. S.**, The microbial production of methane from the putrescible fractions of sorted household waste, in *Proc. Int. Symp. 1st Recycling World Cong.*, Henstock, M. E., Ed., Basel, Switzerland, 1978.
169. **de Baere, L. and Verstraete, W.**, High-rate anaerobic composting and biogas recovery, *BioCycle*, 25, 30, 1984.
170. **Nyns, E. J. and Pauss, A.**, Production of methane by anaerobic digestion of domestic refuse, in *Proc. Int. Symp. Anaerobic Digestion and Carbohydrate Hydrolysis of Waste*, Luxembourg, 1984, 30.
171. **Ishida, M., Odawara, Y., Geyo, T., and Okumara, H.**, Biogasification of municipal waste, in *Recycling Berlin '79*, Thomé-Kozmiensky, K. J., Ed., Freitag-Verlag für Umwelttechnik, Berlin, 1979, 797.
172. **de Baere, L. and Verstraete, W.**, Anaerobic fermentation of semi-solid and solid substrates, in *Anaerobic Digestion and Carbohydrate Hydrolysis of Waste*, Ferrero, G. L., Ferranti, M. P., and Naveau, H., Eds., Elsevier Applied Science Publishers, London, 1984, 195.
173. **Augenstein, D. C., Wise, D. L., and Cooney, C. L.**, Packed bed digestion of solid wastes, *Resour. Recov. Conserv.*, 2, 257, 1977.
174. **Rijkens, B. A. and Voetberg, J. W.**, Two-step process for anaerobic digestion of solid wastes, in Proc. 2nd Int. Symp. Anaerobic Digestion, Travemunde, FRG, 1981.
175. **Walter, D. K.**, Anaerobic digestion of municipal solid waste to produce methane, in *Recycling International: Recovery of Energy and Material from Residues and Wastes*, Thomé-Kozmienky, K. J., Ed., Berlin, 1982, 206.
176. **Diaz, L. F. and Trezek, G. J.**, Biogasification of a selected fraction of municipal solid wastes, *Compost Sci.*, 18(2), 8, 1977.
177. **Gerletti, M.**, Anaerobic digestion of M.S.W. improved by other organic wastes in large pilot plants, in *Anaerobic Digestion and Carbohydrate Hydrolysis of Waste*, Ferrero, G. L., Ferranti, M. P., and Naveau, H., Eds., Elsevier Applied Science Publishers, London, 1984, 446.
178. **Ghosh, S., Conrad, J. R., and Klass, D. L.**, Anaerobic acidogenesis of wastewater sludge, *J. Water Pollut. Control Fed.*, 47, 30, 1975.
179. **Naveau, H., Beckers, G., Legros, A., and Nyns, E.-J.**, Production of Methane by Anaerobic Digestion of Domestic Refuse in a Two Step Process, Abstr., Society for General Microbiology, 107th Meet., Swansea, 1986, 30.
180. **Wentworth, R. L.**, Anaerobic digestion in North America, in *Anaerobic Digestion and Carbohydrate Hydrolysis of Waste*, Ferrero, G. L., Ferrenti, M. P., and Naveau, H., Eds., Elsevier Applied Science Publishers, London, 1984, 348.
181. EEC, General statistics, *Biomass News Int.*, 1, 17, 1984.
182. **Gandolla, M., Grabner, E., and Leoni, R.**, Possibilities of gas utilisation with special emphasis on small sanitary landfills, *Experientia*, 38, 209, 1982.
183. **Senior, E. and Balba, M. T. M.**, Landfill biotechnology, in *Bioenvironmental Systems*, Vol. 2, Wise, D. L., Ed., CRC Press, Boca Raton, FL, 1987, chap. 2.
184. **Mouton, C., Beckelynck, J., Albagnac, G., and Dubourguier, H. C.**, Production and recovery of biogas from household waste landfills, *Tech. Sci. Munic.*, 80, 391, 1985.
185. **Raab, J.**, Biogas resources developed in Oregon, *Public Works*, 116(7), 64, 1985.
186. **Moss, H. D. T.**, Commercial exploitation of landfill gas, *Wastes Manage.*, 75, 172, 1985.
187. **Zimmerman, R. E. and Walsh, J. J.**, Landfill gas utilisation feasibility study, *Public Works*, May, 75, 1984.
188. **Blachet, M. J.**, Recovery and utilisation of biogas at Mountain View landfill, *Ing. Ambientale*, 10, 500, 1981.
189. **Tabasaran, O.**, Methane recovery from municipal waste in landfills, *Trib. CEBEDEAU*, 35, 483, 1982.
190. **Vanni, A.**, Quantitative assessment of the productive capacity and the possibilities of biological methane capture and extraction from municipal solid waste (MSW) landfills, *Ing. Ambientale*, 10, 504, 1981.
191. **Crutcher, A. J., Rovers, F. A., and McBean, E. A.**, Methane gas utilization from landfill site, *J. Energy Div. Proc. Am. Soc. Civ. Eng.*, 107, 95, 1981.
192. **Bogardus, E. R.**, New strategies for biogas recovery, *BioCycle*, 22, 30, 1981.
193. **Parker, D. and Bradshaw, A. D.**, Another look at Liverpool, *Landscape Design*, 161, 32, 1986.
194. **Nosanov, M. E. and White, R. L.**, Gas control and beneficial use of completed landfills, *Public Works*, Nov., 62, 1975.
195. **Wood, J. A., Porter, M. L., and Wadley, M. W.**, Toxics in Class II landfill gas, *Am. Chem. Soc. Div. Environ. Chem.*, 26, 347, 1986.

Chapter 6

LANDFILL CO-DISPOSAL

Irene A. Watson-Craik

TABLE OF CONTENTS

I. Introduction 160

II. Generation and Disposal of Hazardous Wastes 161

III. Co-Disposal of Hazardous Wastes 166
- A. Emplacement 166
- B. Attenuation 166
  - 1. Immobilization 167
    - a. Refuse Mass Absorption 168
    - b. Refuse/Soil Surface Adsorption 169
    - c. pH Effects 172
    - d. Complexation/Chelation Reactions 172
    - e. Precipitation 173
    - f. Liner Integrity 173
    - g. Isolation of Wastes in Drums 173
    - h. Reducing Conditions 173
    - i. Differential Solubilities 174
    - j. Solidification, Fixation, and Vitrification 174
    - k. Ion-Exchange Capacity 176
  - 2. Unsaturated Zone Attenuation 176
  - 3. Transformation 178
    - a. Photodegradation 178
    - b. Volatilization 178
    - c. Biodegradation 179
- C. Biodegradation Optimization: Site Strategies 179
  - 1. Loading Rate 179
    - a. Organic Loading Rates 179
    - b. Hydraulic Loading Rates 181
  - 2. Mixing 181
  - 3. Segregation 182
  - 4. Leachate Management 182
    - a. Limitation 182
    - b. Treatment 183
    - c. Recycle 184
  - 5. Genetically Engineered Strains 185
  - 6. Strategy Implementation 186

IV. Experimental Design 187

V. Phenolic Wastewater Co-Disposal 192
- A. Single-Stage Model 192