

Monitoring Approaches for Landfill Bioreactors

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Notice

Technical information used in the creation of this document resulted, in part, from a Cooperative Research and Development Agreement (CRADA) between the U.S. Environmental Protection Agency through its Office of Research and Development (ORD) and Waste Management, Inc. Biosites program. Both parties agreed to jointly examine this operational technique for the benefit of the waste management community to better protect human health and the environment. It has been subject to the ORD's internal review process and has been approved for publication as an EPA document.

Foreword

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Sally Gutierrez, Acting Director
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Abstract

Experimental bioreactor landfill operations at operating Municipal Solid Waste (MSW) landfills can be approved under the research development and demonstration (RD&D) provisions of 40 CFR 258.4. To provide a basis for consistent data collection for future decision-making in support of the newly promulgated RD&D requirements, this document outlines an approach for bioreactor landfill monitoring. This document suggests technical guidance only, and is not intended to be used for regulatory purposes. It should also be noted that this document should not take the place of site-specific considerations, nor imply that alternative professional determinations on monitoring and analysis methods are not appropriate. The ongoing research and experience on bioreactor landfill projects have provided the basis for this document; however, advances in monitoring and analysis methods may be identified that warrant future updates to this document.

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Acknowledgment

The authors would like to thank Dr. Timothy Townsend (University of Florida) for his time and valuable input. The authors would also like to thank the following reviewers: Mr. Gary Hater and Roger Green (Waste Management Inc.), Mr. Greg Vogt (SCS Engineering), Mr. David Hansen and other members of the Solid Waste Association of North America (SWANA) bioreactor committee, Bob Phaneuf and other members of Association of State and Territorial Solid Waste Management Officials (ASTSWMO), as well as Dr. K.C. Hustvedt, US EPA Office of Air and Radiation (OAR).

1.0 Introduction and Rational

The U. S. Environmental Protection Agency (US EPA) has conducted field research on the use of landfill bioreactors as a means for managing the nation's solid wastes. This technology has the potential to enhance the rate of degradation of solid wastes and landfill gas energy recovery, and to reduce possible long-term liabilities associated with conventional landfills. Based on research conducted to date, this document identifies key parameters, monitoring frequencies, and testing methods that the Agency believes will be important in the management of landfill bioreactors. The purpose of this document is to assist those responsible for regulatory oversight and the site owner/operators in monitoring bioreactor landfills.

Although the routine use of full-scale bioreactor landfill operations may be limited under current Resource Conservation and Recovery Act (RCRA) Subtitle D regulations, experimental and demonstration bioreactor landfill operations at operating municipal solid waste (MSW) landfills can be approved under the Research Development and Demonstration (RD&D) provisions of 40 CFR 258.4. In association with these provisions, the Agency seeks to have such demonstration operations develop consistent data collection procedures and monitoring so as to support future decision-making under the newly promulgated RD&D requirements. To this end, this document does not make recommendations regarding specific kinds of bioreactor operation techniques rather it outlines recommended approaches (that is, with respect to monitoring parameters, sampling frequencies, and sampling procedures) for bioreactor landfill monitoring. The ongoing research and experience on bioreactor landfill projects have provided the basis for this document; however, advances in monitoring and analysis methods may be identified that warrant future updates to this document.

This document suggests technical guidance only, and is not intended to be used for regulatory purposes. It should also be noted that this document should not take the place of site-specific technical and regulatory considerations, or alternative professional determinations on monitoring and analysis methods that may be appropriate. Finally, it is the responsibility of the owner/operator of a landfill to comply with all existing local, state and federal regulations with regard to controlled operations of the landfill.

2.0 Document Organization

This document outlines key parameters for monitoring landfill bioreactors. Approaches are recommended with regard to sampling parameters to be considered, sampling and analytical frequencies, and appropriate standard test methods. A list of bioreactor landfill references has been developed for the reader.

Parameter lists are presented in two categories: physical and analytical. The analytical parameters are divided based on the matrix of interest (liquid, solid, gas). Approaches are provided for those parameters considered vital for understanding bioreactor landfills, including recommendations for those parameters that are relatively inexpensive and simple to measure while maintaining operational control.

Due to the heterogeneous nature of municipal solid waste, variability in waste streams, between landfills and differences in environmental and climate conditions, the use of control cells is encouraged. For research and demonstration purposes the control cells should be comparable in age, depth, and composition of waste, and should be monitored separately to demonstrate impacts of bioreactor landfill operations on volumes and quality of leachate and landfill gas generated, changes in the waste mass, and effects on the leachate collection system. Note that, while it is believed that the use of control cells associated with bioreactor landfill proposals would be beneficial and improve upon the data base being established, it is understood that the use of control cells may not be feasible in all cases.

3.0 Anaerobic Decomposition Fundamentals

A MSW landfill does not have a single waste age, but rather different ages associated with the various cells within the landfill and their respective stabilization stages (Pohland et al. 1993). As a result, the different landfill stabilization phases often overlap. These phases are usually viewed collectively which tends to limit understanding of their progression. Operating a MSW landfill as a bioreactor has an effect only on the rates and not the sequence of the degradation phases (Kim and Pohland 2003; Pohland and Al-Yousfi 1994; Reinhart and Townsend 1998). It is important for those responsible for landfill management to understand each of these events. A brief discussion of the stabilization phases (presented graphically in Figure 1) is presented below. A detailed discussion of landfill stabilization phases has been presented elsewhere (Pohland et al. 1993; Pohland 1975).

3.1 Phase I and II (Initial Adjustment and Transition)

After the initial placement of the waste, a short-lived transition from an oxic to an anoxic microbial stabilization processes, takes place. During that phase, the primary electron acceptors become nitrates and sulfates, rather than oxygen, with the displacement of oxygen by carbon dioxide in the effluent gas additionally, intermediates such as volatile organic fatty acids (VFAs) first appear in the leachate.

3.2 Phase III (Acid Formation)

With the hydrolysis of the biodegradable fraction of the solid waste (and other applied liquids), VFAs concentration in the leachate increase, which results in a decrease in pH. The drop in pH may cause concomitant mobilization and the possible complexation of metal species. During this stage, nutrients such as nitrogen and phosphorous are released from the waste.

3.3 Phase IV (Methane Fermentation)

Intermediary products appearing during the acid formation phase (mainly acetic acid) are converted to methane and carbon dioxide. As a result of VFA consumption by methanogens, the pH drift to neutrality (approximately 7). Oxidation-reduction potentials remain negative indicating a reduced environment. The leachate organic strength (characterized by low biochemical oxygen demand) is dramatically decreased in correspondence with an increase in gas production.

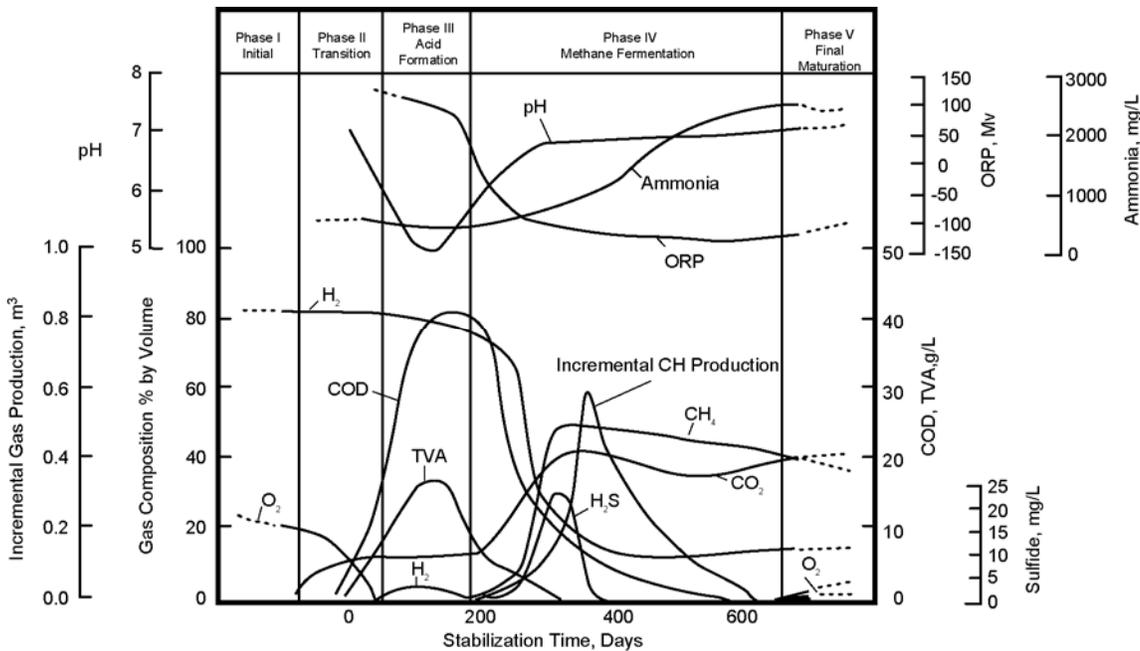


Figure 1: Phases of anaerobic decomposition in MSW landfills (adopted from Pohland and Kim 1999).

3.4 Phase V (Final Maturation)

The final stage of solid waste decomposition is characterized by a lower rate of biological activity. During this stage landfill methane production is almost negligible. Oxygen and oxidized species may slowly reappear with a corresponding increase in oxidation-reduction potential. Residual organic materials may slowly be converted, with the possible production of humic-like substances.

4.0 Key Monitoring Parameters for Bioreactor MSW Landfills

The RD&D (FR 2004) rule allows for the controlled introduction of liquids into a MSW landfill to accelerate the decomposition of biodegradable organics. As briefly discussed earlier, the anaerobic refuse degradation process requires at least two different groups of microorganisms (acidogenic and methanogenic) (Parkin and Owen 1986; Pohland et al. 1993). These microorganisms occur naturally in MSW but require different conditions to achieve optimal performance. There are key parameters, if examined closely, that will collectively ensure the optimal operation of bioreactor landfills and minimize risk to human health and the environment.

Tables 1 through 6 present suggested monitoring parameters for MSW bioreactor landfills which could enhance operational control under RCRA subtitle D and the RD&D (FR 2004) rule. It should be noted that the ranges suggested in this document may not apply to some landfills based on a variety of site-specific factors. It is the responsibility of the owner/operator of a landfill to comply with all existing local, state and federal regulations with regard to controlled operations of the landfill.

Table 1. Mass Loading Calculation Parameters

Parameter	Frequency	Units
Visual Landfill Inspection	Daily	
Mass of Landfilled MSW	Daily	MG (tons)
Mass of Landfilled Construction and Demolition Waste	Daily	MG (tons)
Mass of Soil (other than daily cover)	Daily	MG (tons)
Type of Daily Cover	Daily	
Mass of Daily Cover	Daily	MG (tons)
Landfill volume	Quarterly	m ³ (yd ³)
Settlement	Quarterly	m (ft)

Table 2. Bioreactor Liquid Addition Monitoring Parameters

Parameter	Frequency	Units
Volume of Leachate Added	Daily	L (gal)
Rainfall	Daily	Mm (inch)
Volume Outside Liquid Added (e.g., Groundwater, Industrial Waste Water)	Daily	L (gal)
Volume of Leachate Generated	Daily	L (gal) of leachate generated by the bioreactor cells only
Mass of Sludge Added	Daily	Mass (tons)
Wet Basis Moisture Content of Sludge Added	Daily	Percent (M/M)

Table 3. Primary Bioreactor Landfill Leachate Monitoring Parameters

Parameter	Method	Frequency	Optimum Range ^ε
Static head on Liner	Pressure Transducer. Bubble Gages. Stand pipes.	£	< 30 cm (1ft)
Temperature	Thermometer	Monthly	30 – 38 °C
pH	EPA [¥] 9045C	Monthly	6.5 – 8.0
Conductance (µSm/cm)	Field Electrode	Monthly	§
Total Dissolved Solids (mg/L)	SM [¥] 160.1 (C)	Monthly	§
Alkalinity (mg/L as CaCO ₃)	SM [¥] 310.1	Monthly	§
Chloride (mg/L)	SM [¥] 300.1	Monthly	§
Bromide (mg/L)	SM [¥] 300.1	Monthly	§
Fluoride (mg/L)	SM [¥] 300.1	Monthly	§
Sulfate (mg/L)	SM [¥] 300.1	Monthly	§
Chemical Oxygen Demand (mg/L)	SM [¥] 410.4	Monthly	§
Biochemical Oxygen Demand (mg/L)	SM [¥] 405.1	Monthly	§
Total Organic Carbon (mg/L)	EPA [¥] 9060	Monthly	§
Total Phosphorous (mg/L)	SM [¥] 365.2 (C)	Monthly	§
Ortho Phosphate (mg/L)	SM [¥] 365.2 (C)	Monthly	§
Ammonia (mg/L)	SM [¥] 350.1 (C)	Monthly	< 5,000 mg/L
Nitrite (mg/L)	SM [¥] 300.1	Monthly	§
Nitrate (mg/L)	SM [¥] 300.1	Monthly	§

[£] Head on the liner should be monitored continuously, however, it is suggested that a weekly average is reported.

[¥] EPA SW-846 Test Methods for Evaluating Solid Wastes

[¥] EPA Methods for Chemical Analysis of Water and Wastes.

^ε Landfill owner operator is responsible for following all existing local, state and federal regulations.

[§] Data are currently unavailable. More research is needed.

Table 4. Secondary Bioreactor Landfill Leachate Monitoring Parameters

Parameter	Method	Frequency
Volatile Organic Compounds ^a (VOCs) (µg/L)	SW-846 8260 (B)	Quarterly
Semi-Volatile Organic Compounds (SVOCs)	SW-846 8270 (B)	Quarterly
Volatile Fatty Acids (mg/L)	GC MS	Quarterly
Arsenic (mg/L)	SW-846 6010(prepared per SW-846 3005)	Quarterly
Barium (mg/L)	SW-846 6010 (prepared per SW-846 3005)	Quarterly
Cadmium (mg/L)	SW-846 6010 (prepared per SW-846 3005)	Quarterly
Calcium (mg/L)	SW-846 6010 (prepared per SW-846 3005)	Quarterly
Copper (mg/L)	SW-846 6010 (prepared per SW-846 3005)	Quarterly
Chromium (mg/L)	SW-846 6010 (prepared per SW-846 3005)	Quarterly
Iron (mg/L)	SW-846 6010 (prepared per SW-846 3005)	Quarterly
Lead (mg/L)	SW-846 6010 (prepared per SW-846 3005)	Quarterly
Magnesium (mg/L)	SW-846 7470 (prepared per SW-846 3005)	Quarterly
Mercury (µg/L)	SW-846 7470 (prepared per SW-846 3005)	Quarterly
Potassium (mg/L)	SW-846 6010 (prepared per SW-846 3005)	Quarterly
Sodium	SW-846 6010 (prepared per SW-846 3005)	Quarterly
Selenium (mg/L)	SW-846 6010 (prepared per SW-846 3005)	Quarterly
Silver (mg/L)	SW-846 6010 (prepared per SW-846 3005)	Quarterly
Zinc (mg/L)	SW-846 6010 (prepared per SW-846 3005)	Quarterly

^a Constituents listed in 40 CFR 258 Appendix I.

Table 5. Bioreactor Landfill Solids Monitoring Parameters

Parameter	Method	Frequency	Optimum Range ^e
Average Temperature	Thermometer	Once every 18 months	35 - 55 °C
Average pH	EPA ^a 9045C	Once every 18 months	6.5 - 7.6
Average Volatile Solids (% M/M)	EPA ^b 1684	Once every 18 months	Decreasing Trend
Average Wet Based Moisture Content (% M/M)		Once every 18 months	< 35 %

^a (EPA, 2003)

^b (Mehanta et al., 2002)

^e Landfill owner operator is responsible for following all existing local, state and federal regulations.

Table 6. Primary Bioreactor Landfill Gas Monitoring Parameters

Parameter	Flow	Frequency	Optimum Range ^e
Total Gas	Orifice plate / Mass flow meter (scfm)	At least once a week	
Carbon Dioxide	Portable gas analyzer (% V/V)	Weekly	35-40
Oxygen	Portable gas analyzer (% V/V)	Weekly	< 5
Methane	Portable gas analyzer (% V/V)	Weekly	45 – 60
Carbon Monoxide	Portable gas analyzer (% V/V)	Weekly	≈ 0

4.1 Physical Monitoring Parameters

4.1.1 Geotechnical Considerations

Landfill slope stability is an important parameter in MSW landfill design. Often landfill slope stability focuses on the stability of the final landfill configuration. Operating landfills as bioreactors may add more strain on slope stability, not only of the final configuration but also on the interim slopes. Pore pressure in bioreactor landfills may potentially increase because of the addition of liquids and the concurrent increase in landfill gas (LFG) generation. As a result, it is important to conduct a detailed geotechnical analysis of the slopes stability of each bioreactor landfill.

In conjunction with a slope stability study, operators could follow simple guidelines to promote bioreactor landfill slope integrity. Operators should avoid toe excavation that, if left unbuttressed, could create high stress and may potentially cause a slide. Operators should also avoid filling waste in cells at steep grades. On-site roads and cover soil may also lead to instability, thus requiring care with design.

4.1.2 Head on Liner and Leachate Management

As required under CFR 258, leachate head on a landfill bottom liner is not to exceed 30 cm (1 ft). The addition of moisture into the landfill will cause excess amounts of leachate to reach the bottom liner. Before the addition of moisture into a bioreactor landfill, an engineer should ensure that the leachate collection system (LCS) design can handle the increase in leachate flow. Performance of the LCS and removal systems relative to clogging also should also be examined.

Potential clogging of the LCS may lead to moisture buildup within the landfill causing the head on the liner to exceed 30 cm and create potential leakage and instability issues. Alkalinity, hardness, iron, manganese compounds, total organic carbon,

chemical and biological oxygen demand, are all involved in reactions which can result in buildup of clogging material in leachate collection systems (Cooke et al. 2001; Fleming et al. 1999; Rittmann et al. 2003; Rowe et al. 2000). These parameters can indicate how closely leachate concentrations are to saturation levels for calcium carbonate and other compounds that contribute to clogs and poor LCS efficiencies. LCS clogging could be caused by settling out of suspended particles from the leachate, biological growth, or chemical precipitation (Koerner and Koerner 1995).

4.1.3 Mass Balance

It is important for those responsible for the management of bioreactor landfills to keep records of the mass of the landfilled solid waste in each bioreactor cell. Conducting surveys for volume on a regular basis can be helpful in estimating the density of solid waste placed. As the solid waste decomposes the density of the landfill tends to increase. Parameters that may assist with mass loading calculations are presented in Table 1. Visual inspection is also included in Table 1. Although visual inspection does not assist with mass loading calculation, physical investigation of landfill surface may identify wet, soft areas that may be precursors to sideweeps and fugitive gas escape zones. Both conditions may require prompt correction.

To minimize perched leachate zones within the landfill, efforts must be made to remove temporary roadways as well as daily cover prior to waste placement. Thus, the use of tarps or foams as an alternate cover to soil is encouraged. If soil is used as daily cover, soil type should also be noted (e.g., clay or sand) and it should be removed prior to the placement of fresh waste.

4.1.4 Moisture Balance

The main premise of operating a landfill as a bioreactor is the introduction of moisture into the landfill. Up to a point, the decomposition and stabilization rate of biodegradable solid wastes increases with increasing moisture content of that waste. Although research has shown the optimum moisture content for biological degradation to range between 30 and 70 percent (Pohland et al. 1993; Reinhart and Townsend 1998), an increase in landfill moisture content tends to decrease the landfill's side slopes stability (see section 4.1.1). Moisture plays an important role in side slopes stability landfill moisture content needs to be examined regularly.

Assuming the volume of water consumed during waste hydrolysis and evaporation are negligible; moisture balance can be calculated as presented in the following equation:

$$\Delta S = \text{Moisture}_{\text{in}} - \text{Leachate}_{\text{out}} \quad (1)$$

Where “ ΔS ” is the net moisture storage, “ $\text{Leachate}_{\text{out}}$ ” is the leachate generated by the landfill and “ $\text{Moisture}_{\text{in}}$ ” is all liquids added into the landfill including precipitation. Moisture addition could occur in many different forms including, but not limited to, leachate, and municipal and industrial waste water addition. Parameters assisting in maintaining a water balance are presented in Table 2. It is also important to take into account the moisture content of the incoming waste.

4.2 Analytical Monitoring Parameters

4.2.1 Leachate Monitoring

Suggested leachate monitoring parameters for MSW bioreactor landfills to enhance operational control under RCRA and the RD&D (FR 2004) rule are divided into primary (Table 3) and secondary parameters (Table 4). The primary parameters are relatively inexpensive and easy to examine. Parameters presented in the secondary list are more research-oriented, and are more time intensive and as a result are relatively costly. Suggested analysis methods and monitoring frequencies are presented in the tables. It is the responsibility of the owner/operator of a landfill to comply with all existing local, state and federal regulations with regard to existing monitoring parameters in addition to parameters agreed upon under an RD&D project. A few monitoring parameters are evaluated further in the following sections.

Sample duplication is necessary to account for the statistical relevance of monitoring data. Caution must also be taken to hydraulically isolate bioreactor from adjacent conventional landfill cells. The separation would allow for an accurate evaluation of conditions only within the bioreactor. Hydraulic separation may be achieved in an as-built cell; however, such a separation is more difficult in retrofit bioreactor landfill cells. In the case of a retrofit bioreactor landfill, it is suggested that the zone of influence of the liquid application area be examined (see Reinhart and Townsend, 1998 for more details). Leachate samples representing the bioreactor section of the landfill should be collected only from areas directly under the zone of influence.

4.2.1.1 Leachate Temperature

Research suggests that anaerobic processes occur best within either mesophilic (30-38°C) or thermophilic (50 to 60°C) temperature ranges (McCarty 1964; Parkin and Owen 1986). Optimum methane generation from solid wastes, however, occurred

at 41°C (Harts et al. 1982). Regardless of the operational temperatures, the maintenance of a uniform temperature is considered to be fundamental to anaerobic stabilization process efficiencies. Historically, conventional landfills leachate temperature ranged from 7 to 25°C while bioreactor landfills leachate ranged from 6 to 37°C (EPA 2003).

Because landfill temperature is not externally controlled, it reflects a combination of ambient temperature conditions, microbial activities and the extent and effectiveness of insulation provided by the landfill configuration. In cold climates, for example, leachate temperatures could initially be as low as 6°C. Soon after recirculation the leachate temperatures should steadily increase. Leachate temperatures at the Outer Loop landfill in Kentucky were initially around 7°C. The leachate temperatures at the landfill steadily increased to above 30°C within a few months of the bioreactor operation (EPA 2003). While an increase in leachate temperature is reflective of waste degradation in a landfill, it is not solely indicative of biological activity.

4.2.1.2 Leachate pH

The optimum pH range for anaerobic systems ranges between 6.5 and 7.6 (Parkin and Owen 1986). Gas generation and stabilization rates have been reported to be the highest at near neutral pH levels (Pohland et al. 1993). Initially the leachate pH may be neutral, however after the onset of anaerobic conditions there may be a pH drop especially during the acid forming phase (see section 3.2). The pH drop is most likely caused by VFAs production and accumulation in the leachate. The pH, however, will tend to move to neutrality as methanogens consume these acids. Historically there may not be a measured difference between the leachate pH measured in conventional and in bioreactor landfills. The leachate pH ranged between 4.7-8.8 for conventional landfills (EPA 2003; Kjeldsen et al. 2002; Chu et al. 1994; Krung and Ham 1991) and from 5.4-8.6 for bioreactor landfills (EPA 2003; Pohland and Harper 1986).

There may be a sudden drop in pH following a single injection event of highly degradable industrial waste water (as observed at the Outer Loop landfill). The decrease in pH should last for approximately a week depending on the volume of liquid added. Repetitive injection events can prolong the change in pH. It is important not to allow the pH to be suppressed for long periods of time since low pH inhibits methanogens, reducing waste degradation (see section 5).

4.2.1.3 Volatile Fatty Acids (VFA)

An uncontrolled bioreactor landfill is characterized by acidic leachate (high volatile fatty acids content) and a low methane production for a prolonged period. Bioreactor leachate becomes acidic as a result of the accumulation of VFAs (acetic, propionic, butyric, hexanoic and valeric acids). For more detailed discussion of VFAs see (Barlaz et al. 1989; Kim and Pohland 2003; Pohland et al. 1993).

4.2.1.4 Leachate Biochemical (BOD) and Chemical Oxygen Demand (COD)

BOD mainly consists of the biologically degradable dissolved organics in the landfill leachate. The ratio of BOD to COD can potentially be used to assess the relative biodegradability of the leachate substrate. COD is a measure of chemically oxidizable organics in leachate. Variations in these two parameters may be closely related to those observed with VFAs production and their ratio can act as an indicator of the biodegradability of organics present in the MSW. BOD values reported in the literature for conventional landfills ranged from 20 to 152,000 mg/L (EPA 2003; Pohland and Harper 1986a; Kjeldsen et al. 2002; Chu et al. 1994; Krung and Ham 1991). The reported BOD values for bioreactor landfills ranged from 20 to 28,000 mg/L (EPA 2003; Reinhart and Townsend 1998; Miller et al. 1994; Pohland et al. 1993). COD values ranged from 500 to 60,000 mg/L for conventional landfills (EPA 2003, Reinhart and Townsend 1998, Miller et al. 1994, Pohland et al. 1993).

Immediately after waste placement, the BOD and COD concentrations are relatively low. This may be caused by the initial aerobic stabilization of the MSW or by a delay in the hydrolysis of the waste. During the acid formation phase, the majority of the oxygen demand (both BOD and COD) is caused by the presence of high concentration of VFAs.

BOD and COD concentrations may decrease after the onset of the methane fermentation phase and the conversion of VFAs. Relative to conventional landfills, bioreactor landfills may have a higher BOD/COD ratio during the acid forming phase (Reinhart and Al-Yousfi 1996; Reinhart and Townsend 1998). However, research suggests this ratio may decrease during the methane fermentation phase. After waste stabilization, both BOD and COD may be influenced by high molecular weight organics present in the leachate (e.g. humic and fulvic) (Pohland et al. 1993). These residuals tend to elevate COD to a higher level than BOD and possibly reduce the BOD/COD ratio. For instance, leachate BOD/COD ratios are usually higher than 0.5 for acid formation phases of decomposition but may decline to less than 0.1 for heavily decomposed waste. It is noted that COD is also influenced by the increase in ammonia concentration.

4.2.1.5 Leachate Total Organic Carbon (TOC)

In general, like COD and BOD, after the initial placement of the waste TOC begins to appear as a result of microbial solubilization of the organics. During the acid forming phase, TOC increases rapidly. An increase in TOC may also be observed soon after the introduction of highly organic liquid waste. Because of the conversion of the VFAs to methane, TOC concentration tends to decrease during the methane fermentation phase. TOC of conventional landfills ranges between 30 and 30,000 mg/L (Chu et al. 1994; EPA 2003; Kjeldsen et al. 2002; Krung and Ham 1991; Pohland and Harper 1986).

4.2.1.6 Leachate Nitrogen Content

Nitrogen is present in MSW leachate mainly in the following forms: total Kjeldhal nitrogen (TKN), ammonia nitrogen, and nitrate nitrogen. Ammonia is most important since at high concentrations (1,500 - 2,500 mg/L) it tends to inhibit methanogens (Hansen et al. 1998; Hashimoto 1986), reducing waste degradation. Under anaerobic conditions ammonia tends to accumulate in the leachate, especially with recirculation. Increasingly higher concentrations of ammonia in leachate may indicate potential for adverse effects on the methanogenic population, but it is also a sign of advanced stage of waste decomposition. High ammonia concentrations may be used to decide when to stop recirculating leachate.

While conventional landfill leachate ammonia concentrations range from 2 to 2200 mg/L (EPA 2003; Pohland and Harper 1986a; Krung and Ham 1991), that of bioreactor landfills range from 6 to 20,000 mg/L (EPA 2003; Reinhart and Townsend 1998; Miller et al. 1994; Pohland et al. 1993). Care must be taken so the accumulation of ammonia in the leachate does not adversely affect the methanogenic population.

4.2.1.7 Metals

Metal concentration in the leachate is an important parameter to examine and can affect the cost of off-site leachate treatment. The lower pH and higher organic content of the leachate during the initial landfill stabilization phases may mobilize some metals during the acid forming phase (Pohland et al. 1993; van der Sloot and Woelders 2000). However, after the onset of the methane fermentation phase, metal concentrations tend to decrease. The reduction in these concentrations is caused by a combination of metal reduction, formation of metal sulfides, precipitation, and complexation with the waste matrix. The introduction of large concentrations of heavy metals, through solid or liquids, may retard or inhibit solid waste degradation process stabilization (Pohland and Harper 1986).

4.2.1.8 Semi-Volatile and Volatile Organic Compounds (SVOCs, VOCs)

Analysis of SVOCs and VOCs are of particular importance since there is a potential for the introduction of complex organic constituents into bioreactor landfills with the application of various industrial wastes. Bioreactor landfills' ability for microbial assimilation and transformation of organic, and potentially toxic, compounds has been documented (Kim and Pohland 2003). In-situ reductive dehalogenation of organic compounds (e.g., TCE and HCB) has been demonstrated in bench-scale bioreactor landfill studies (Kim and Pohland 2003). Monitoring of less attenuated organic compounds, as well as daughter products, in the leachate is an essential part of operating a controlled bioreactor landfill.

Monitoring data are needed to assess which of the VOC and SVOC compounds are most likely to appear in leachate, in what concentration ranges, over what time periods, and whether their behavior is different from their behavior in conventional landfills.

4.2.1.9 Phosphate

Phosphate may possibly be the rate controlling micronutrient in landfill environments. The addition of phosphates as a beneficial micronutrient to laboratory-scale bioreactor landfill cells has been documented (Sheridan 2002). This practice, however, has not been further examined in the field.

4.2.2 Solids Monitoring Parameters

Unlike leachate and gas, it may also be physically difficult and expensive to obtain samples of waste. Due to the difficulty in sampling and the time it takes for decomposition to affect waste properties, this document recommends a lower sampling frequency as presented in Table 4. Suggestions for drilling and sampling methods are discussed in a later section.

Temperature monitoring of the waste surface should be conducted much more frequently than temperature of the interior of the waste mass. Temperature on the waste surface and at shallow depth may be monitored daily, as well as indications of smoke and heat, carbon monoxide, and other signs of combustion and lack of moisture. Inspections and monitoring of these parameters are needed to assure safety, prevent damage to the liner and collection system, and determine where additional water is needed to moderate temperatures and moisture deficiencies.

Note that, while it is believed that solids monitoring is scientifically beneficial and adds to the data base being established, it is understood that solid sampling as suggested in this document may not be feasible.

4.2.2.1 Volatile Solids

As stated earlier, moisture addition stimulates biological activity in bioreactor landfills. This increase may directly translate to an increase in the degradation of cellulose and hemicellulose and an increase in the settlement rate. A three-year study at Yolo County landfill (California) demonstrated that the cellulose, hemicellulose and lignin content is strongly correlated to the volatile solids (VS) content of MSW (Mehanta et al. 2002). It is recommended that bioreactor landfill operators/owners examine the refuse content of cellulose, hemicellulose and lignin on a regular basis (once every 18 months). Such a practice may be cost prohibitive, thus VS analysis may substitute as a potential degradability indicator. The main disadvantage of using VS is that, unlike cellulose, hemicellulose and lignin, the analysis offers a lower level of accuracy and is affected by daily cover application. Bioreactor operator/owner should expect MSW VS content to decrease as the refuse decomposes because of cellulose and hemicellulose content loss from the waste.

4.2.2.2 Moisture Content

The moisture content of the decomposing solid waste should be examined to insure equal distribution of the liquids added to the bioreactor landfill. The moisture content of the “fresh” incoming solid waste needs to be evaluated as well to establish baseline measurements. Moisture content of the incoming waste plays a major role in the moisture balance calculations which may be used in slope stability evaluation.

4.2.3 Gas Monitoring Parameters

During the solid waste biodegradation process, landfills generate measurable quantities of methane and carbon dioxide (both are undesirable greenhouse gases). Controlling and monitoring the emissions of these gases is an essential element of any controlled landfill operations. The rate of landfill gas production at bioreactor landfills is estimated to be between two (Reinhart and Townsend 1998) and ten (Mehanta et al. 2002) times higher than that at conventional landfills. With that in mind, bioreactor landfill gas collection systems need to be designed to handle larger flow rates than conventional landfills. It may also be necessary to begin gas collection in bioreactor landfills earlier than the 180 days required under the National Emissions Standards for Hazardous Air Pollutants (NESHAP) regulations (40 CFR part 63, subpart AAAA).

One of the regulatory concerns associated with bioreactor landfills has been concern for the potential for subsurface fires from spontaneous combustion. Literature suggests that carbon monoxide is a useful indicator of subsurface fires. Monitoring carbon dioxide is useful both in determining if carbon monoxide concentrations in bioreactor landfill gas are typical of what would be seen in conventional landfill gas and as an indicator for subsurface fires (Sperling and Hendersons 1996).

As with conventional landfills, methane constitutes between 15 and 60% of bioreactor landfill gas. Carbon dioxide comprises approximately 35-40 % of the gas while the oxygen content should be lower than 5%. Nitrogen comprises the balance of the landfill gas.

It may be necessary to measure landfill gas emission at the flare and also fugitive gas emissions using a static flux chamber. The Flux chamber test may be rather expensive, however, it will give important data regarding the flux ($\text{mg}/\text{m}^2/\text{sec}$) through the surface of the landfill. Methane, carbon dioxide, and none-methane organic compounds could be measured at the flare and surface emissions may be measured using a flux chamber on the bioreactor landfill. EPA TO-14A compounds may also be examined. See applicable NESHAP (40 CFR part 63, subpart AAAA) regulations regarding bioreactor landfills for more details.

5.0 Interim Industrial Liquids/Sludge Addition Issues

The RD&D (FR 2004) rule gives landfill owners/operators latitude in the types of liquids (including industrial waste water and sludges) to be introduced into bioreactor landfills. Ultimately, the owner/operator of a landfill has the final responsibility to insure that the addition of industrial liquids or sludge does not inhibit the degradation process and is compliant with existing state and federal regulations. Little is known about interactions between industrial waste liquids and bioreactor landfill operations, so general liquids selection criteria are presented here based on the limited research experience at the Outer Loop landfill in Kentucky and other sites. The following sections will outline general selection criteria for industrial liquid/sludge addition to bioreactor landfills. Note, bioreactor landfill operations require the addition of aqueous liquids, rather than oily or petroleum-based liquids. Liquids containing petroleum-based fuels should not be introduced into a bioreactor landfill.

5.1 pH

The strength of the acid or base plays a large role in determining the compatibility of the liquid waste with the refuse in the MSW landfill. Because pH is a sensitive parameter in the anaerobic decomposition process, liquid waste with an acidic pH (pH <4.0) should not be introduced to a landfill unless the liquid can be neutralized prior to addition. Liquid waste with a basic pH may be introduced, however, these liquids should be injected over a large area so that they are readily neutralized. It is assumed that MSW landfills have the buffering capacity to better accommodate basic liquids (pH > 9). Field tests on a waste specific basis are highly encouraged. Testing may be as simple as adding the liquid waste of interest to a small controlled area of refuse and performing extractions and pH measurements over time. An example liquid waste stream is beverage waste (e.g., soft drinks, etc). This particular liquid waste contains high concentrations of organic compounds with a low pH. Finally, if there are liquid waste streams that may be constant in composition for longer periods of time (weeks or months), then some laboratory testing could be done to measure the waste alkalinity or acidity to characterize its strength (EPA 2003).

5.2 Organic Compounds Content

There are two potential issues with the addition of industrial waste containing high levels of organic compounds. The first is the introduction of rapidly fermentable organic compounds and the second is the potential toxicity of some organic compounds.

Liquids that contain rapidly fermentable compounds will likely be acidic or will result in a local accumulation of carboxylic acids when added to refuse. As explained earlier, acidic conditions may have an adverse, in some cases inhibitory, impact on refuse decomposition. If the application of liquids containing rapidly fermentable organic compounds is still desired, the liquids should be applied at a low rate and only to refuse that is either in a methane fermentation state or to well decomposed refuse. A good practice would also involve blending of new waste streams with recirculated leachate.

Although toxicity is chemical specific, the addition of high concentrations of organic pollutants has been shown to retard refuse decomposition. The long-term effect of organic pollutants on refuse decomposition is still unclear, however. If organic pollutants present in the waste are known, a simple literature search could determine whether that pollutant is toxic and/or biodegradable in an anaerobic environment. If there is a liquid stream for which no data are available, laboratory toxicity test may be required. A lab test on liquid being added to waste mass is advisable to see if methane is inhibited at various liquids to mass ratios.

Although all liquid waste streams should be characterized before landfill application, the following waste streams are particularly problematic and should not be allowed into bioreactor landfills: surfactant based waste streams, waste streams containing oily or petroleum fuels, pickling wastes streams, streams related to aluminum dross, and waste streams with high sulfate concentrations.

5.3 Metals

Under the RD&D (FR 2004) rule the addition of non-hazardous heavy metals bearing liquids is permitted but discouraged. High metal content has been observed to retard the onset of the methane fermentation phase and even inhibit methane production altogether (Pohland and Harper 1986). Care must be taken to insure residence time, within the landfills, to allow metal attenuation.

6.0 Suggested Sampling Techniques

The following sections outline suggested sampling techniques. Comparable sampling techniques may be employed if necessary.

6.1 Leachate Sampling

Landfills receive a wide variety of wastes from municipal, agricultural and industrial sources. As a result leachate composition varies significantly not only among different geographical regions but also within different cells at the same landfill. Sample duplication is necessary to account for the statistical relevance of monitoring data. Caution must also be taken to hydraulically separate bioreactor cells from adjacent conventional landfill cells. The separation would allow for an accurate evaluation of conditions only within the bioreactor. Hydraulic separation may be achieved in an as-built cell; however, such a separation is more difficult in retrofit bioreactor landfill cells. In the case of retrofit bioreactor landfill, it is suggested that the zone of influence of the liquid application area be examined (see Reinhart and Townsend, 1998 for more details). Leachate samples representing the bioreactor section of the landfill should be collected only from areas directly under the zone of influence.

A common practice at most landfills is to pool the leachate generated at the facility at one sump prior to pumping for treatment or recirculation. As a result leachate from various areas of the landfill (bioreactor areas and conventional) is mixed. Leachate sampling should not occur at central sumps, but rather at a point before bioreactor leachate is mixed with that of conventional landfill cells. Operating a particular landfill as a bioreactor is highly discouraged unless leachate generated by the bioreactor cells is sampled separately. The inability to do so would prohibit accurate assessment of biological activity and moisture loading calculation in the landfill bioreactor, which may result in operational problems.

Atmospheric interactions may cause a change in leachate temperature, pH and total solids after sampling. To minimize these effects temperature and pH measurement should be taken immediately at the point of leachate sampling.

6.2 Solid Waste Sampling

6.2.1 Waste Sampling for New Cells

This particular sampling process is mainly used at newer bioreactor landfills. This procedure is also used with newly placed (within two weeks of initial placement) waste (EPA 2003). A transect line is created along the length and in the center of the area of the landfill to be sampled. The transect line is further divided into five equally spaced sections and these sections are surveyed. Samples are collected using a backhoe at a depth of three feet and six feet at each location for a total of ten samples.

MSW temperature may be measured using a long-stemmed thermometer (e.g., meat thermometer) as the waste is brought to the surface and recorded. The pH of the MSW may also be measured using, for example, a “pocket pen” pH meter (available from a number of scientific supply houses). A one-liter plastic container is filled halfway with MSW. Distilled water is added to the MSW until it just covers the refuse. The mixture is shaken for approximately two minutes and the pH of the mixture is then measured and recorded.

After measuring the temperature and pH, each sample is placed in a plastic bag. Each bag is then sealed and placed in a five gallon pail with a sealable lid. Care must be taken to expel excess air from the bags after placement of the waste. A tag attached to the bag should contain important information such as the landfill name, address, date, and sample coordinates from the survey. Similarly, a label should be placed on the outside of the pail to ensure no confusion arises in the laboratory. Samples collected could be analyzed for moisture content, volatile solids, cellulose, hemicellulose, and lignin content (EPA 2003).

6.2.2 In-place Waste Sampling

This procedure is used for as-built (except for the baseline sampling outlined in section 6.2.1) and retrofit bioreactor landfills (EPA 2003). MSW samples are collected using a bucket auger. Boring locations should be surveyed, labeled with coordinates and safe drilling depth. Drilling should be avoided within 3 m (10 ft) from the bottom liner.

One shovel of MSW is sampled from each auger brought to the surface of the landfill. These “shovel” samples are mixed to make a composite MSW that represents 1.5 m (5ft) intervals. For example, a composite sample would represent MSW augured between 3 and 5 m (10 and 15 ft). Sample handling as well as temperature and pH measurements follows the same methodology outlined in section 6.2.1.

6.3 Gas Sampling

Gas sampling should follow National Emissions Standards for Hazardous Air Pollutants (NESHAP) requirements (40 CFR part 63, subpart AAAA). The requirements include extensive monitoring of the well head gas to ensure proper collection and periodic surface monitoring for leaks, cracks and fissures or under-designed collection systems.

References

- Barlaz, M., Ham, R., and Schafer, D. (1989). "Mass-Balance Analysis of Anaerobically Decomposed Refuse." *Journal of Environmental Engineering*, 115(6), 1088-1102.
- Chu, L., Cheung, K., and Wong, M. (1994). "Variations in the Chemical Properties of Landfill Leachate." *Environmental Management*, 18(105-114).
- Cooke, A., Rowe, R., Rittmann, B., VanGulck, J., and S., M. (2001). "Biofilm Growth and Mineral Precipitation in Synthetic Leachate Columns." *Journal of Geotechnical and Geoenvironmental Engineering*, 10(127), 849-856.
- US. EPA, (2003). "Landfills as Bioreactors: Research at the Outer Loop Landfill, Louisville, Kentucky. First Interim Report." US Environmental Protection Agency, Cincinnati, Oh.
- Fleming, I., Rowe, R., and Cullimore, D. (1999). "Field Observations of Clogging in a Landfill Leachate Collection System." *Canadian Geotechnical Journal*, 36, 685-707.
- Hansen, K., Angelidaki, I., and Ahring, B. (1998). "Anaerobic Digestion of Swine Manure Inhibition by Ammonia." *Water Research*, 32(1), 5-12.
- Harts, K., Klink, R., and Ham, R. (1982). "Temperature Effects: Methane Generation from Landfill Samples." *Journal of Environmental Engineering*, 108(4), 629-638.
- Hashimoto, A. (1986). "Ammonia Inhibition of Methanogenesis from Cattle Wastes." *Agricultural Wastes*, 17, 241-261.
- Kim, J., and Pohland, F. (2003). "Process Enhancement in Anaerobic Bioreactor Landfills." *Water Science and Technology*, 48(4), 29-36.
- Kjeldsen, P., Barlaz, M., Rooker, A., Baun, A., Ledin, A., and Christensen, T. (2002). "Present and Long-Term Composition of MSW Landfill Leachate: A Review." *Critical Reviews in Environmental Science and Technology*, 32(4), 297-336.
- Koerner, G., and Koerner, R. "Long-Term Permeability of Granular Drainage Material." *Proceedings Seminar Publication Landfill Bioreactor Design and Operation*, Wilmington, DE.
- Krung, M., and Ham, R. "Analysis of Long-Term Leachate Characteristics." *Sardinia International Landfill Symposium*, Cagliari, Italy, 9-12.
- McCarty, P. (1964). "Anaerobic Waste Treatment Fundamentals." *Public Works*, 9-12.
- Mehanta, R., Barlaz, M., Yazdani, R., Augenstein, D., Bryars, M., and Sinderson, L. (2002). "Refuse Decomposition in the Presence and Absence of Leachate Recirculation." *Journal of Environmental Engineering*, 128(3), 228-236.
- Parkin, G., and Owen, F. (1986). "Fundamentals of Anaerobic Digestion of Wastewater Sludges." *Journal of Environmental Engineering*, 112(5), 867-920.
- Pohland, F., and Al-Yousfi, B. (1994). "Design and Operation of Landfills for Optimum Stabilization and Biogas Production." *Water Science and Technology*, 30(12), 117-124.
- Pohland, F., Cross, W., Gloud, J., and Reinhart, D. (1993). "Behavior and assimilation of organic and inorganic priority pollutants co-disposed with municipal refuse." *EPA/600/R-93/137a*, Risk Reduction Engineering Laboratory Office of Research and Development, Cincinnati, OH.
- Pohland, F., and Harper, S. (1986). "Retrospective evaluation of the effects of selected industrial wastes on municipal solid waste stabilization in simulated landfills." 234.

- Pohland, F., and Kim, J. (1999). "Insitue Anaerobic Treatment of Landfills for Optimum Stabilization and Biogas Production." *Water Science and Technology*, 40(8), 203-210.
- Pohland, F. G. (1975). "Sanitary landfill stabilization with leachate recycle and residual treatment." *EPA-600/2-75-043*, U.S. Environmental Protection Agency, Cincinnati, Ohio.
- Reinhart, D., and Al-Yousfi, B. (1996). "The Impact of Leachate Recirculation on Municipal Solid Waste Landfill Operating Characteristics." *Waste Management and Research*, 14, 337-346.
- Reinhart, D., and Townsend, T. (1998). *Landfill Bioreactor Design and Operation*, Lewis Publishing, New York.
- Rittmann, B., Banaszak, J., Cooke, A., and Rowe, R. (2003). "Biogeochemical Evaluation of Mechanisms Controlling CaCO₃(s) Precipitation in Landfill Leachate Collection Systems." *Journal of Environmental Engineering*, 129(8), 723-730.
- Rowe, K., Armstrong, M., and Cullimore, D. (2000). "Particle Size and Clogging of Granular Media Permeated with Leachate." *Journal of Geotechnical and Geoenvironmental Engineering*, 126(9), 775-786.
- Sheridan, S (2002). *Modeling Solid Waste Settlement as a Function of Mass Loss*, Master Thesis, University of Florida. Gainesville Fl.
- Sperling, T., Hendersons, P. (1996) "Understanding and Controlling Landfill Fires." *6th Annual Landfill Symposium*, San Diego, California, 367-377.
- van der Sloot, H., and Woelders, H. "Leaching Behaviour of ESSENT Bioreactor Rest Product at Different Stages of Degradation in Lab and Pilot Scale to Assess Potential Utilization Options." *Symposium Lulea*, Sweden.