

Gas Generation at a Municipal Waste Combustor Ash Monofill - Franklin, New Hampshire

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INTRODUCTION

The characterization of landfill gas generated at municipal solid waste landfills has received significant attention in the United States in recent years. Generation of gas at municipal waste combustor (MWC) ash monofills is, however, generally assumed to be negligible and there is little, if any, published information available concerning such gases. As ash landfills move towards closure in the future, and as progress continues in utilizing certain components of MWC ash residue in construction applications, it is important to identify the mechanisms by which gases may be generated in MWC ash so that appropriate design and material management decisions can be made.

This information is based upon the analysis of gas samples from leachate collection system cleanout pipes at one lined MWC ash landfill. The data were gathered because site operating staff had posed questions as to the contents of the gaseous emissions. The gas characteristics indicated the effects of exothermic chemical reactions in the landfilled ash which affected gas composition in ways which were unexpected, and not widely known.

PROJECT BACKGROUND

The lined MWC ash landfill in Franklin, New Hampshire is owned by the 27 member municipalities of the Concord, NH Regional Solid Waste/Resource Recovery Cooperative ("the Cooperative"). The landfill was initially constructed in 1988, and has operated continuously since 1989.

The landfill accepts combined bottom ash, fly ash and dry lime scrubber product from the 500 ton per day waste to energy (or Municipal Waste Combustor) facility in Concord, New Hampshire owned and operated by a subsidiary of Wheelabrator Technologies, Inc. The MWC facility processes about 177,000 tons per year of municipal solid waste and generates about 68,000 wet tons per year of combined ash. Bottom ash is discharged from the combustion units into wet ash troughs, from which the bottom ash is removed by means of drag chain conveyors. The facility's air pollution control system consists of pneumatic injection of hydrated lime directly into the exhaust gas ductwork for control of acid gas emissions, with fabric filters for control of particulates. The fly ash and dry lime scrubber product is treated with the proprietary WES-PHix process, and combined with the bottom ash on the bottom ash drag chain conveyor. The WES-PHix process involves the addition of phosphoric acid (H_3PO_4) to the fly ash to promote the formation of lead phosphates, in order to limit the solubility of lead in the ash.

The lined MWC ash landfill in Franklin, New Hampshire consists of a double lined landfill with a primary leachate collection system consisting of HDPE piping above the primary (or uppermost) liner. The leachate collection pipes discharge to leachate tanks at the low side of the site, from which leachate is pumped to a remote sewer connection. The leachate tanks are vented to the atmosphere.

Since the primary leachate collection pipes beneath the landfilled ash flow only partially full, air/gas can flow through the pipes with intake at the leachate collection tanks at the low side of the site. Air flows through the primary leachate collection pipes and discharges through the leachate system cleanout pipes located on the high side of the site, through a "chimney" type effect.

The landfill is designed to reach a final maximum depth of about 120 feet. In 1996, residue grades were about 45 feet above the landfill liners. In order to facilitate future leachate collection needs at higher

elevations, two leachate collection pipes had been extended vertically through the fill. One of these two pipes had been perforated every several feet and wrapped with geotextile fabric. During a storm event, ash deposited in the perforated vertical pipe had clogged the bottom 1.5 feet where the pipe connected to the leachate collection pipe. This clogged pipe had a water surface within the pipe, thus closing off convective air access to the leachate collection system. A cross section of this vertical pipe is presented as Figure 1. In this condition, this one vertical pipe inadvertently functioned as a typical landfill gas well. This clogged vertical pipe is noted as the "Phase 1 Vent".

An initial evaluation of the gas was made by Cooperative staff using a handheld explosivity meter ("LEL meter"), on the various cleanouts and leachate collection pipe outlets (or "vents"). The meter's alarm was tripped at two of the outlets for elevated H₂S concentration, and the alarm for lower explosive limit ("LEL") exceedance was tripped for the Phase 1 Vent. This information led the Cooperative to decide to sample and analyze the gaseous emissions.

Ash Characteristics

There are a number of factors pertaining to the specific ash handled at the Franklin site and the operating scheme at the landfill which may affect the generation of gas. These characteristics and the potential impacts of each are listed and discussed below.

- **Ash Combustible Content** - A comprehensive ash sampling and analysis program conducted in 1990 and 1991 indicated that the bottom ash at that time had a combustible content averaging 6.4% as measured by Loss on Ignition tests (3). This combustible content may be considered moderate to high by US standards. This may have affected non-methane organic compound concentrations.
- **Lime Content** - The direct dry lime injection system requires the addition of lime at 2 to 4 times the stoichiometric requirement for acid gas control. This rate is higher than at most plants with more stoichiometrically efficient spray dryer absorption systems. The ash at Franklin may have greater alkalinity and unreacted lime than is typical of other ash monofills. The primary leachate, however, has had a pH of 7 or below for the past seven years.
- **Phosphoric Acid Addition** - Small amounts of phosphoric acid are added to the fly ash/scrubber product using the proprietary "WES-PHix" process. The addition of phosphoric acid has been considered in terms of its potential to have an effect on gas generation. Any effect is presumed minimal due to the neutralization of phosphoric acid by the lime.
- **Landfill Operating Scheme** - The Franklin ash landfill is operated aggressively as a "dry tomb" type of facility in comparison to most US landfills. The limited amount of time (2-3 years), during which the landfilled ash has been subjected to percolation of water may have an effect on chemical reactions taking place in the landfill.

Other than those factors described above, the ash generated by the Concord, New Hampshire waste to energy facility is considered to be typical of most US facilities based on the type of facility, operation and ash characterization data available.

Landfill Piping Configuration

The specific layout of the various vents is depicted schematically on Figure 2. The nomenclature for

each gas sampling point, and the specific circumstances of each location are presented in Table 1 below.

Gas Temperature and Flows

The landfill interior temperature was measured by lowering a weighted thermocouple into the Phase 1 and Phase 2 vents. Phase 2 pipes were not clogged, but were open to air/gas flow from the leachate collection system below. Ambient air temperature at the time of sampling was 39°F.

The Phase 2 vent could be measured only 9 feet down the pipe due to the presence of a bend. The temperature was 91°F. Gas in this vent was diluted by atmospheric air from the leachate collection system below.

The temperature of undiluted gas in the clogged Phase 1 vent ranged from 132°F to 156°F. The temperature profile with depth is indicated on Figure 3. These temperatures were unexpectedly high and were higher than would typically be expected in an MSW landfill. Optimum temperatures for thermophilic anaerobic digestion of MSW range from 120° to 135°F (4). It is postulated that the elevated temperatures are likely due to a variety of exothermic, primarily inorganic chemical reactions taking place in the landfilled ash.

Measured gas flows are as indicated on the piping schematic presented as Figure 2. A chimney effect is apparent as pipes open to the atmosphere at lower elevations indicated flow into the piping system and the vents connected to the piping system which outlet at higher elevations emitted gas at flows of 20 and 28 cubic feet per minute (CFM). Gas flows at the Phase I vent were estimated to be 30 to 60 CFM. This flowrate is similar in magnitude to the rate which might be experienced at steady state conditions in an active MSW landfill gas well. The zone of influence within the landfill mass of the Phase 1 vent is unknown.

MWC Landfill Gas Characteristics

The vents which had exhaust flow to the atmosphere were sampled and analyzed for atmospheric gases, non-methane organic compounds (NMOCs) and sulfur compounds. Samples were gathered using evacuated SUMMA passivated (polished) canisters with samples withdrawn over a 60 minute duration, per Method TO14. Atmospheric gases were analyzed by GC/FID/TCD using ASTM Method D-3416. NMOCs were analyzed by gas chromatograph/pyrolysis CO₂ using Method TO12 (total NMOC), and by gas chromatography/mass spectroscopy for the full Method TO14 target compound list. Sulfur containing compounds were quantified through ASTM Method 5504.

The summary of the atmospheric gas analyses is presented in Table 2. The oxygen content in the Phase 2 Vent and the Phase 1 Upper Cleanout, both of which were open to atmospheric air in the leachate collection pipes beneath the landfill, were near typical atmospheric levels. The oxygen content in the Phase I Vent, which was clogged and functioning in a way similar to a gas well, was markedly depressed, but not absent. Methane was present in the Phase I Vent at a concentration of 780 ppm. This is low compared to the levels present in gases from MSW landfills (typically 500,000 ppmv, or 50%), and at a level well below the lower explosive limit (LEL) for methane of 50,000 ppmv. If methanogenic bacterial activity was at a high level, the O₂ concentration in the Phase 1 Vent would have been expected to approach zero, and the CO₂ concentration would have been much greater.

Hydrogen was detected in the gas in the Phase 1 Vent. The hydrogen concentration in both Phase 1 Vent samples was measured to be 5.1%, which is in excess of the 4.0% LEL for hydrogen. The presence of

hydrogen at these concentrations is likely the cause of the explosiveness alarm in the initial gas screening described earlier. The hydrogen is postulated to be generated by oxidation reduction reactions of aluminum and other reactive metals, and/or other chemical reactions, taking place within the landfill mass, as discussed later herein.

Hydrogen sulfide concentrations were elevated in the Phase 2 Vent and in the Phase 1 upper cleanout, as indicated in Table 3. H₂S is typically a by-product of the anaerobic decomposition of organic matter. The H₂S concentrations are likely indicative of microbial activity within the landfill mass.

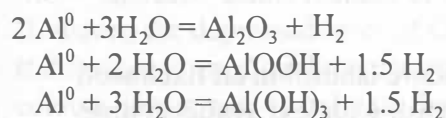
The NMOC concentrations are presented in Table 3. The NMOC concentrations were present at the low end of the range of concentrations reported in the literature (4) for NMOC concentrations in MSW landfill gas. Leachate from the landfill site rarely has detectable concentrations of volatile organic compounds with the exception of periodic low concentrations of acetone.

The concentrations of specific organic compounds were reported for two samples from the Phase 1 Vent and for one sample from the Phase 2 Vent. The results are presented in Table 4. The reported concentrations are all lower than presently applicable health and safety related standards and are generally less than those anticipated in MSW landfill gas (5).

Following the completion of the sampling and analysis described herein, the clog in the Phase 1 vent was removed hydraulically. Later LEL meter testing indicates that the Phase 1 and Phase 2 vents subsequently have similar characteristics.

Discussion of Results and Implications

Generation of Hydrogen Gas. The measured hydrogen gas may be generated by chemical reactions of elemental aluminum and other elemental metals in the presence of water. Typical oxidation reduction reactions may be as follows (6,7):



The aluminum reactions are facilitated in the presence of either strong acids or strong bases, which may etch the surface of the aluminum, exposing more elemental aluminum to the reaction. In typical uses of aluminum subject to atmospheric exposure, an adherent protective film of aluminum oxide forms on the surface of the aluminum in pH conditions in the range of 4 to 9 (8). This protective surface film precludes further corrosion of the underlying aluminum. However, in the presence of strong acids or bases, this film may be destroyed and the hydrogen gas generating corrosion reactions can continue. When the protective film is destroyed (or the aluminum is "depassivated"), the exposed elemental aluminum reacts vigorously in the presence of moisture until all exposed aluminum is reacted. The protective oxide film reforms within seconds of exposure of elemental aluminum (15), which limits the length of time that aluminum corrosion continues to occur in atmospheric exposure.

In the landfill, the conditions under which corrosion occurs are more complicated. The aluminum is present both in bulk form and in fine particles, and the chemical conditions which affect corrosion vary locally throughout the landfill mass. Aluminum corrosion can be facilitated by the presence of chloride ions (17), which are present in abundance in MWC ash. The chloride ions affect the aluminum through

pitting, exposing additional elemental aluminum to the corrosion reaction. The chemistry of aluminum is complex, and the reactions taking place in the heterogeneous landfilled residue are not well understood.

Aluminum is present in significant quantities in the ash. Bottom ash from the Concord, New Hampshire MWC facility has a range of aluminum content of 3.4 to 6.4% by weight. Aluminum is also typically present in fly ash in significant concentrations. It is anticipated that a significant percentage of the aluminum present in the ash exists in the elemental form having the potential for the hydrogen generating oxidation reduction reactions.

Hydrogen gas may also be generated by similar reactions with other elemental metals. The oxidation of elemental aluminum, zinc, chromium, iron, copper and other elemental metals can proceed in the proper environmental conditions, releasing electrons. The electrons, in the presence of water and, again, in the proper environmental conditions, can result in the generation of H₂ gas. The aluminum reaction is highlighted herein because of the redox potential of the aluminum reaction, the significant quantity of aluminum in the ash, and the likely presence of elemental aluminum in greater quantities than is likely for the other elemental metals. Oxidation reduction reactions of many elemental metals probably contribute to varying extents to the H₂ gas generation.

Hydrogen is also generated as a byproduct in certain organic decomposition reactions (i.e., in the later stages of anaerobic, non-methanogenic decomposition in an MSW landfill (4)), and can be generated as a byproduct in a variety of other chemical reactions.

It is considered unlikely that the addition of phosphoric acid plays a significant role in hydrogen gas generation at the landfill site. Although the Material Data Sheet supplied by the phosphoric acid supplier warns of the hydrogen gas generation potential when in contact with aluminum, this is due to the acidic nature of the phosphoric acid. The H₃PO₄ acid is neutralized at the MWC facility upon mixing with the highly alkaline scrubber product.

The unusually high alkalinity of the fly ash at the Franklin, New Hampshire landfill in all likelihood results in greater hydrogen gas generation than would be the case for an ash with less available lime. Hydrogen gas at other sites should still be anticipated to be present, although likely at a slower generation rate.

The hydrogen gas generating reactions of aluminum have been known for many years, and have been used in the manufacture of lightweight concrete with a cellular structure (13, 14). Aluminum powder is added to cement and sand. In the presence of lime or other alkali, hydrogen bubbles are formed throughout the concrete, creating a more porous structure. The practice is more prevalent in Europe than in North America.

Anecdotal information is available regarding experience with the generation of hydrogen gas from MWC ash. Fly ash utilized as an aggregate substitute in asphalt cement in Germany developed gas bubbles during paving (11). The gas was analyzed and found to be primarily hydrogen. The generation of hydrogen gas and methane from fly ash and scrubber residue has been documented in laboratory studies in Germany (11, 12). Explosions in a fly ash system in Denmark were attributed to hydrogen gas (15, 16). Explosive conditions were subsequently prevented through ventilation of ash conditioning equipment.

The presence of hydrogen gas at levels above the LEL is not believed to be a major risk factor with respect to landfill operations. Landfill gas from MSW landfills often exhibits methane concentrations above the LEL and below the upper explosiveness limit, at concentrations where explosions could occur in certain circumstances. This risk is managed by proper gas handling in passive or active gas collection systems at closed landfills and by appropriate monitoring of gas concentrations at the site periphery to assure that subsurface migration to nearby structures does not occur. If the generation of hydrogen gas is confirmed at other ash landfill sites, similar design and operation precautions would likely be appropriate for ash landfills as well. Appropriate precautions should be taken when excavating into ash in confined spaces, or when drilling into old landfilled ash.

The potential for generation of hydrogen gas should be considered when evaluating ash utilization alternatives. Until further information is developed, the utilization of unencapsulated ash in close proximity to confined spaces such as structures may be inadvisable. Some researchers (11) have suggested that the aging of ash prior to utilization might be effective in reducing the potential for hydrogen gas release after utilization. The length of time required and the effectiveness of any reduction in subsequent gas generation are not yet known.

- **Ash Temperature**

The elevated temperature determined within the landfill mass is most likely due to a variety of exothermic chemical reactions. Preliminary, theoretical thermodynamic calculations indicate that neither the exothermic aluminum reactions described herein nor the lime hydration reactions would be expected, alone, to generate sufficient heat to bring the landfilled mass to the 156°F maximum temperatures measured. Other exothermic chemical reactions also undoubtedly play a role.

In the peer review process, for this paper, a reviewer commented that high temperatures and carbon monoxide concentrations greater than 100 ppm are generally indicative of combustion conditions in MSW landfills. Some manner of combustion may have been occurring in the ash at the Franklin site. However, the depressed level of CO₂, which is generated in most combustion processes and is generally stable once formed, and the presence of hydrogen gas, which would likely not be present in the midst of combustion, appear to indicate that combustion is not a major factor in the formation of the gases sampled.

From a design standpoint, the elevated ash temperature is not significantly problematic. Temperatures in the ranges measured do not negatively affect most flexible membrane liners and geotextile materials typically used in landfill construction. The design of leachate collection pipes is somewhat temperature dependent in that the calculation of the pipe wall material's modulus of elasticity requires temperature input, depending upon the type of pipe used. Until valid information is developed from other sites indicating the prevalence of much lower ash temperatures, the use of 160°F as the temperature input in leachate collection pipe strength calculations, where required, may be advisable.

- **Provisions for Gas Management in Ash Landfill Closure Designs**

It is apparent from the information reported upon herein that gas management provisions need to be incorporated in the design for closure of an MWC ash landfill. Design procedures similar to those utilized for the closure of smaller MSW landfills with passive gas venting systems may be appropriate. The installation of a suitable gas migration layer beneath impervious capping materials, and passive vents through impervious capping layers, should be, and typically are, incorporated in closure designs.

Further information is needed regarding the movement of gas within landfilled ash to determine whether passive gas wells within the ash are needed or are otherwise of benefit.

• **Additional Information Needs**

Information is needed from other ash landfills to confirm the temperature of ash at depth, and to assess hydrogen gas generation rates and concentrations. Both the temperature and the hydrogen gas generation rates may be lower at other sites where less lime is available for hydration reactions. It should be noted that the hydrogen gas concentrations measured at any site are less a function of generation rate than they are a function of the site's tendency to accumulate gases. The data reported upon herein provides no information regarding the nature of gas pressure and concentration gradients within an ash monofill.

The effect of aging the ash prior to utilization with regards to the subsequent generation of hydrogen gas also deserves investigation.

CONCLUSIONS

The following conclusions can be drawn from the information reported upon herein:

1. MWC ash disposed in an ash monofill may generate gas with NMOC concentrations on the low end of the typical range for NMOCs in MSW landfill gas.
2. Gas flowrates generated in an ash monofill may be significant from a closure design perspective.
3. Hydrogen gas may be generated within the ash mass at an ash monofill from reactions of elemental aluminum and/or from other sources. Hydrogen gas concentrations may exceed the lower explosive limit.
4. Ash temperatures within an MWC ash monofill may be on the order of 156°F, due to reactions of elemental aluminum, lime hydration reactions and other exothermic chemical reactions. The potential for elevated temperatures should be considered in the design of landfill components.
5. Anaerobic non-methanogenic and methanogenic decomposition of waste does not appear to be a significant factor in the generation of gas at an ash monofill, despite the presence of an uncombusted fraction in the ash.
6. Lower ash temperatures and decreased rates of generation of hydrogen gas may be experienced at other ash landfills having less lime available for hydration reactions than was present in the ash at the Franklin, New Hampshire site. However, elevated temperatures and some hydrogen gas generation should be anticipated until experience indicates otherwise.
7. Passive gas vents, and effective gas migration layers beneath impervious caps, should be incorporated in designs for closure of ash monofills.
8. Appropriate precautions should be taken when excavating into ash in confined spaces, or when drilling into old landfilled ash.
9. The potential for generation of hydrogen gas should be considered in ash utilization programs.

Until further information is developed otherwise, the utilization of unencapsulated ash in close proximity to enclosed spaces (i.e., structures) may be inadvisable. The potential benefit of aging of ash on reducing subsequent hydrogen gas generation in utilization merits investigation.

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Table 1. Gas Sampling Locations.

Sampling Point	Type of Pipe	Depth of Ash	Age of Ash
Phase 1 Vent	Perforated, Clogged at Depth (Similar in Function to Gas Well)	42 feet	0-4 years
Phase 2 Vent	Solid Wall, Open to Leachate System Below (Diluted by air flow from below)	46 feet	1-2 years
Phase 1 Upper Cleanouts	Solid Wall, Open to Leachate System Below (Diluted by air flow from below)	54 feet	4-8 years

Table 2. Summary of Atmospheric Gas Analyses.

Location	Oxygen (%)	Nitrogen (%)	Carbon Monoxide (ppm)	Methane (ppm)	Carbon Dioxide (%)	Hydrogen (%)
Phase 1 Vent						
first (can 3)	3.5	91	110	780	.008	5.1
second (can 4)	3.6	91	110	780	.008	5.1
Phase 2 Vent						
first (can 1)	21	79	<20	<20	.038	.087
second (can 2)	21	79	<20	<20	.038	.092
Phase 1 Primary upper cleanout						
first (can 5)	21	79	<20	30	.051	<.024
second (can 6)	21	79	<20	30	.050	<.024

Table 3. Summary of NMOC and Sulfur Gas Analyses.

Location	Non-methane Organic Compounds (ppm)	Hydrogen Sulfide (ppm)	Total Reduced Sulfur (ppm)
Phase 1 Vent			
first (can/bag 3)	38	<0.004	0.290
second (can/bag 4)	40	<0.004	0.270
Phase 2 Vent			
first (can/bag 1)	3.3	11.0	11.0
second (can/bag 2)	4.4	15.0	15.0
Phase 1 Primary upper cleanout			
first (can/bag 5)	0.45	11.0	11.0
second (can/bag 6)	0.48		

Table 4. Summary of Organic Compound Analyses (All reported in ppb).

Compound	Phase 1 Vent Can 3	Phase 1 Vent Can 4	Phase 2 Vent	Typical Concentrations in MSW Landfill Gas ⁽⁴⁾	TLV ² -TWA	STEL ³
Chloromethane	75	110	29	900	50,000	100,000
Methylene Chloride	130	<40	30	19,700	50,000	
Benzene	96	97	<16	3,520	10,000	300*
Toluene	100	93	<16	51,600	50,000	
Acetone	9,900	9,500	1,400	3,360	750,000	1,000,000
Tetrachlorethane	<48	<40	<24	7,040	25,000	100,000
2-Butanone (MEK)	840	720	170	2,800	200,000	300,000
Hexane	1,300	1,200	<65	3,010	50,000	
Ethanol	6,400	5,700	4,200	3,410	1,000,000	
Heptane	690	640	<65	N/A	400,000	500,000
Total Organic Compounds	29,661	22,310	6,179	200,000	N/A	N/A

1 - ACGIH: American Conference of Governmental Industrial Hygienists

2 - TLV-TWA: "Threshold Limit Value - Time Weighted Average" (8 hour work day/40 hour work week, without adverse effect)

3 - STEL: "Threshold Limit Value - Short Term Exposure Limit" (maximum 15 minute exposure)

4 - See Reference 4, USEPA

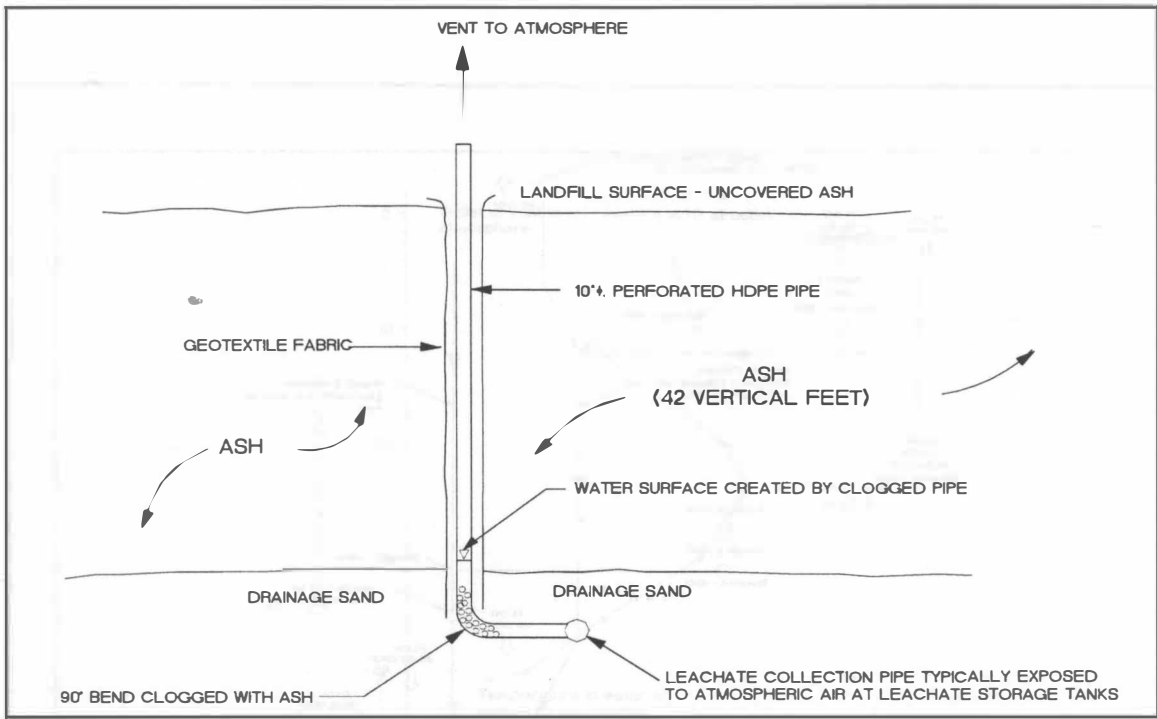


Figure 1. Phase 1 Vent - Cross Section.

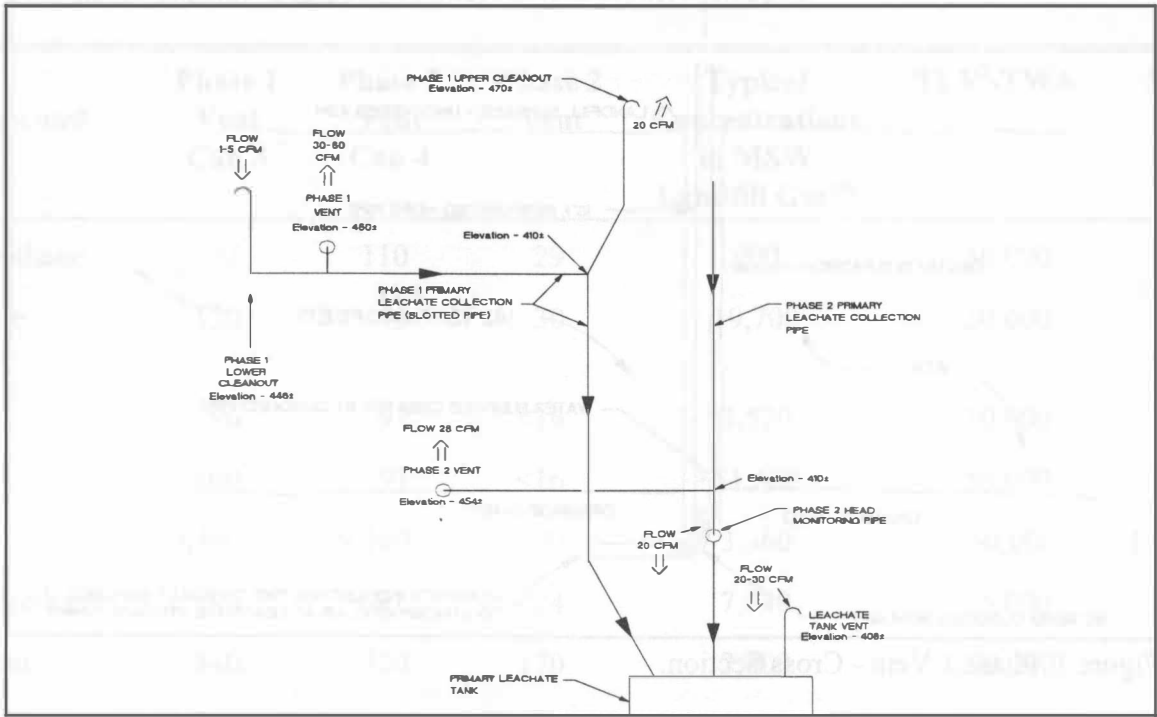


Figure 2. Leachate Collection System Schematic.

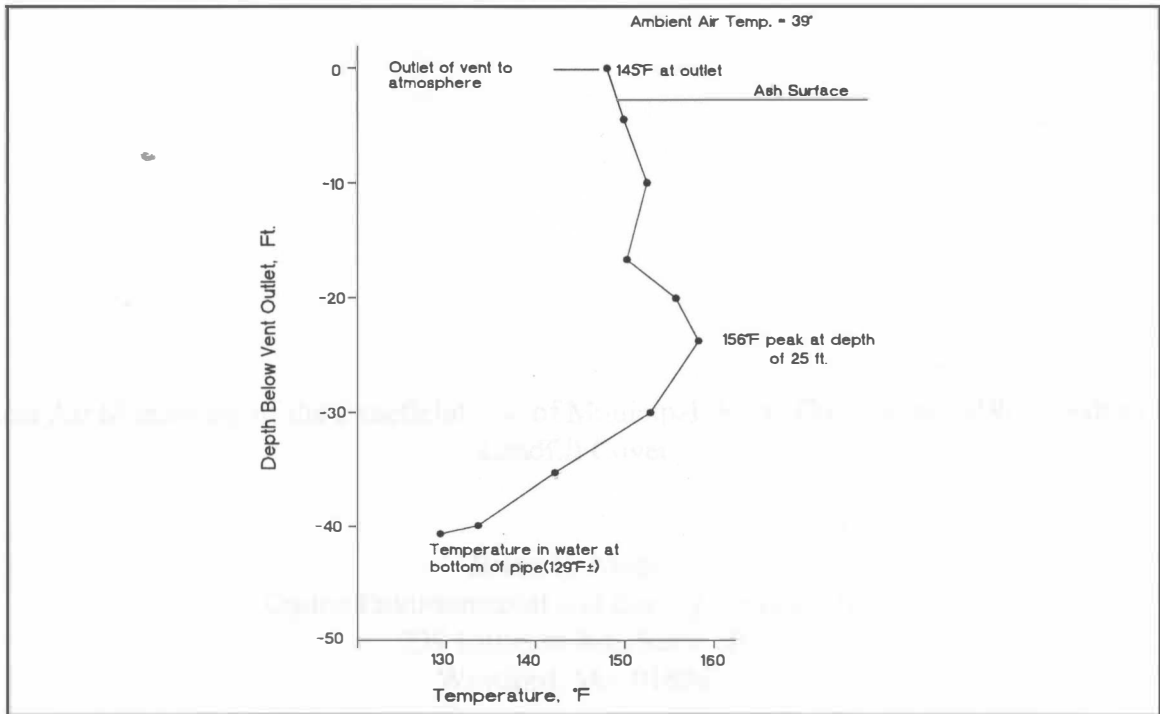


Figure 3. Gas Temperature Profile with Depth.