

A DIFFERENT GAS GENERATING REGIME WITHIN LOW-CARBON WASTE LANDFILLS IN THE UK AND EUROPE

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SUMMARY: In low carbon waste landfills the availability of water or a carbon source, or the build up of toxic compounds appears to limit anaerobic gas generation. Thus oxygen consuming chemical/biological reactions occur immediately after the waste is placed, but factors required for anaerobic degradation become exhausted, perhaps because of limited permeability that also appears to be a feature of this waste. Oxygen and its reaction products, principally carbon dioxide, are removed by phase change from the gas filled pore space of the waste. This results in the proportion of nitrogen in the pore gas rising to more than the 80% typical of atmospheric composition. Nitrogen gas enrichment through oxygen removal can mean either negative pressure within the landfill, or slow air ingress into the waste. New gas management and monitoring techniques at such sites should reflect this different conceptual model.

1. INTRODUCTION

In landfills containing non-inert waste with low-carbon content, chemical reactions may be more important than biological processes for gas generation. This means that for the risk assessment of a landfill containing a low-carbon waste the source term is different from a typical MSW landfill and so current models are not appropriate for these facilities. There appear to have been no systematic studies of the nature and composition of gas accumulating within wastes having a low content of biodegradable carbon. This study aimed to collect representative data that might inform the rational design of gas management infrastructure and monitoring requirements at sites containing low-carbon, non-inert wastes.

In the UK, low-carbon (Hazardous) waste landfills have been operating since 2004, whereas similar landfills have been operating for longer in Europe. To evaluate the composition of gas at such sites, this work sampled the pore gas of 14 low-carbon wastes (4 in Europe), using 8 different sampling media and 11 analytical techniques.

2. SAMPLING AND ANALYSIS

Samples were taken using Teflon[®] lined soil vapour probes driven 1 metre into the emplaced waste at a number of locations in each waste cell. Sampled waste types are shown in Table 2.1.

Table 2.1. Site descriptions

Sites	Waste description
Landfill 1 (UK)	Wide variety of hazardous waste, including metal and solvent waste, but mainly contaminated land and asbestos waste. Temporary cap.
Landfill 2 (UK)	Predominantly hazardous waste generated from remediation of contaminated land including asbestos waste. Compacted cap on top of this waste.
Landfill 3 (UK)	APC residues mixed with water and laid down as slurry. One cell had also taken contaminated land residues. Metre of compacted clay.
Landfill 4A (Europe)	Mixed waste, with the predominant fraction fragmentiser/shredder waste. There is no cover on this cell
Landfill 4B (Europe)	A mixture of wastes that cannot be incinerated, such road sweepings, contaminated land waste etc. This cell has a metre thickness of cover.
Landfill 4C (Europe)	Predominantly bottom ash from incinerators, although other wastes are also present. There is a 1 metre clay cap over this waste.
Landfill 5 (Europe)	Domestic waste that has undergone an intensive aerobic and then anaerobic MBT process. There is no cap on this waste.
Landfill 6 (UK)	Monofilled with metal slag waste 10 years ago. The leachate level is now close to the cap, with a limited unsaturated zone to sample from.
Landfill 7 (UK)	A wide variety of hazardous waste including some slag waste. There is a temporary cap on this waste.
Landfill 8 (UK)	A wide variety of hazardous waste including metal slags. There is no cap on this waste as yet.
Additional phase sites and waste description	
Landfill 1 (UK)	On the second visit a cell that had taken more oily waste was sampled. Sampled leachate well gas and waste next to leachate well.
Landfill 7 (UK)	The other end of the cell sampled previously was sampled on this occasion. Sampled leachate well gas and waste next to leachate well.

Table 2.2. Sample media and analytical suites

Compound	Sample media	Analysis
Nitrogen, oxygen, carbon dioxide, methane	Tedlar [®] bag	Gas Chromatography (GC) – Thermal Conductivity Detection (TCD)
Ethane, propane and butane	Tedlar [®] bag	GC-Flame Ionisation Detection (FID)
Hydrogen and helium	Tedlar [®] bag	GC-TCD
Carbon monoxide	Tedlar [®] bag	Fourier Transform – Infra Red (FT-IR)
Hydrogen sulphide	Tedlar [®] bag	Inductively Coupled Plasma – Atomic Emission Spectroscopy (ICP-AES)
Volatile organics (VOCs)	Dual sorbent ATD tubes	GC-Mass Spectroscopy (MS)
Phosphine	Treated silica gel	ICP-AES
Amines	Treated silica gel	High Performance Liquid Chromatography (HPLC)
Ammonia	Treated silica gel	Ion selective electrode (ISE)
Hydrogen halides	Alkali impinger	Ion chromatography
Hydrogen cyanide	Alkali impinger	Colorimetric measurement
Siloxanes	Tedlar [®] bags	GC-MS
Organo-metals	Nitric Acid impinger	Inductively Coupled Plasma – Mass Spectroscopy (ICP-MS)
Organo-metals	Hydrochloric acid impinger	ICP-MS
Inorganic mercury	Potassium permanganate impinger	ICP-MS
Organic mercury	Potassium bromate impinger	ICP-MS

3. RESULTS

No differential pressure between the gas in the probe and atmosphere was measured at any location. Even at the locations with temporary or permanent capping, there is not enough gas generation to develop a positive pressure relative to atmospheric pressure.

Where two probes were installed within metres of each other at the same depth, the gas composition varied. This suggests that samples are drawn from a low permeability matrix. Gas flow for sampling was difficult to obtain in certain landfills (well-compacted soils, APC residues and bottom ashes). Gas could only be obtained at the waste/cover interface. This may be the only place where there is sufficient gas phase permeability to allow sampling and by implication, gas flow within the waste at these sites.

3.1 Bulk gases

Oxygen and its reaction products appear to be removed by phase change from the pore space of the waste. This results in the proportion of nitrogen in the pore gas rising to more than the 80% typical of atmospheric composition. Nitrogen gas enrichment through oxygen removal can mean either negative pressure within the landfill, or slow air ingress into the waste. Either of these nitrogen gas enrichment scenarios precludes general gas emission from the landfill, because not enough gas is being generated to push out the emplaced atmospheric nitrogen. Of the non-atmospheric gases present in the resultant pore space, biogenic carbon dioxide is low, either because it is easily removed, or is not generated. Biogenic methane and hydrogen, potentially from corrosion or microbial action, are typically detected. Landfills that are not actively gas generating typically have low carbon dioxide concentrations (<6%) and even slowly gassing, uncapped older European landfills seem to contain less than 30% methane.

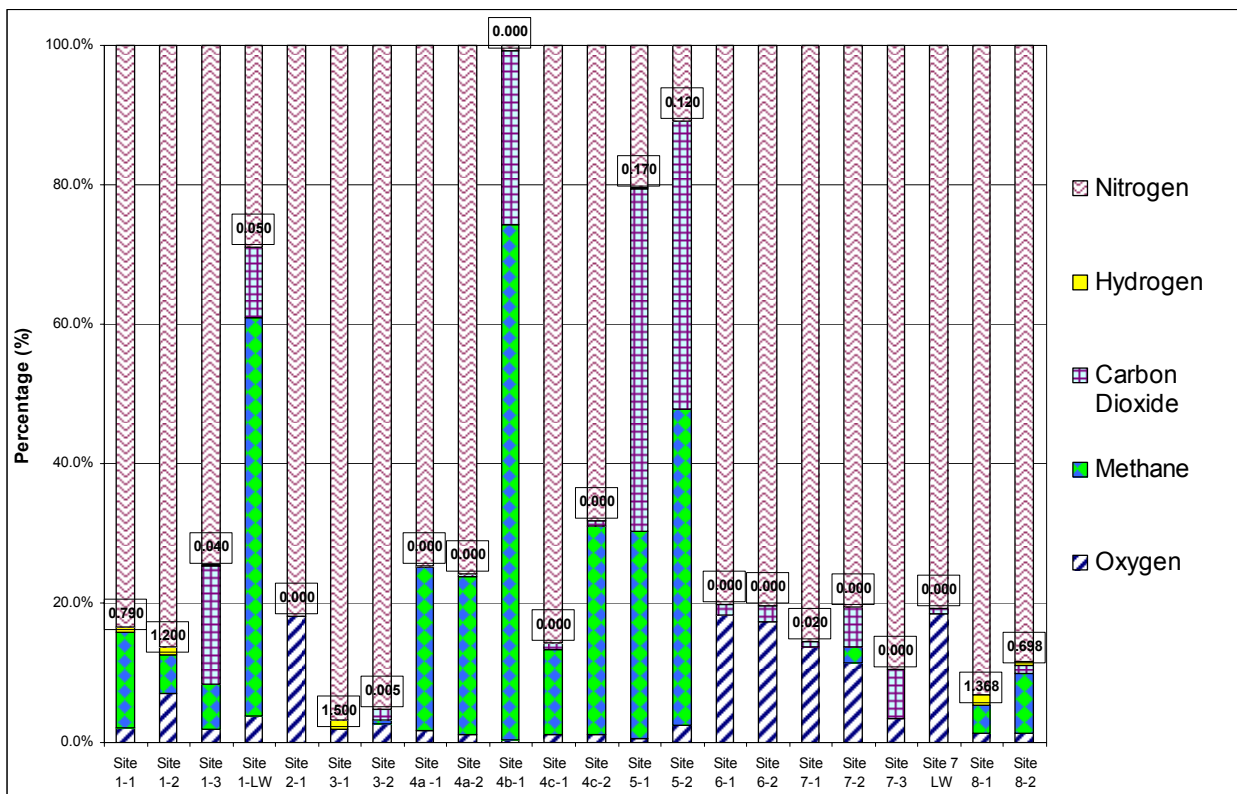
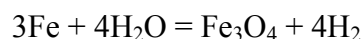


Figure 1. Non-normalised bulk gas data. Hydrogen percentage data in boxes

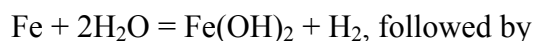
The main source of methane is likely to be from microbial activity degrading carbon based material in the waste under anaerobic conditions. Discounting the fresh waste sites, which may not be representative of steady state conditions, it is interesting that in the landfill containing APC residue with some soil, oxygen and methane co-exist. This may be because there is some other factor that has stopped the activity of oxygen-consuming (or methane-generating) bacteria in this waste. The limiting factor may simply be permeability or moisture. This waste is desiccated and dries the surrounding soil media once emplaced. Such gas composition could indicate that limited gas generating activity occurs immediately after the waste is placed, but it quickly ceases. Slow diffusion would then mix the regions containing methane and air. This presupposes that either air cannot get in and gas cannot get out due to the low permeability of the waste and cap and the low pressures involved, or that the air ingress is balanced by gas being removed from the gas phase.

Although methane concentrations are lower in both more established and low gas production scenarios, carbon dioxide appears to be consumed in preference to methane with ratios increasing up to 118 in Site 4a containing mature waste. In three locations where carbon dioxide is absent, there is considerable hydrogen. At site 3, where the waste is predominantly APC residues, one cell has 1.5% hydrogen and no carbon dioxide, while the other cell (with some soil) has 1.5% carbon dioxide and much lower hydrogen. Another site with relatively high hydrogen concentration (0.7%) is Site 8-1, which has low carbon dioxide (1%). That these two compounds may be related is reinforced by the constant ratio of hydrogen to carbon dioxide (0.003) in 5 further datapoints where both are present, and hydrogen is present at concentrations less than 0.2%. In summary, it appears that where conditions are conducive to hydrogen generation, there is a link between carbon dioxide and hydrogen, with the ratio 0.003 hydrogen to 1 carbon dioxide. Hydrogen concentrations above 0.2 % only occur in the absence of carbon dioxide but in all cases was less than 1.5% in low carbon landfills. This is based on 11 datasets where hydrogen is present.

Carbon based gases are absent in APC-only residue, where the highest hydrogen concentration (15,000 ppmv) is off the scale of the analytical equipment calibration range. Hydrogen generation in point 3-1, in the absence of carbon and sulphate waste and their associated microbial populations, is likely to be chemical. Similarly, hydrogen exists in the absence of methane in hazardous waste at site 7-2. One possible chemical reaction is the corrosion of iron, aluminium and zinc under alkaline or neutral conditions leading to the generation of hydrogen in anaerobic environments:



This consists of two stages (Naish *et al.*, 2001):



The rates of corrosion of all three metals depend on pH, water availability and surface area and may also be influenced by the presence of dissolved species in leachate (e.g. chloride) or physical contact with other metals (galvanic corrosion). Aluminium is potentially quite reactive but is normally coated by a stable layer of oxide, which protects the zero valent metal from attack. In incinerator residues it has been suggested that aluminium oxide residues dissolve in alkaline moisture and only then is hydrogen produced. The absence of water in the APC residue waste at Site 3 may be a key limiting factor to hydrogen production.

3.2 Trace gases

3.2.1 Ethane, propane and butane

Ethane, propane and butane are relatively rare in biogenic landfill gas. They could be produced by:

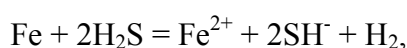
- biological mechanisms such as lipid peroxidation;
- volatilisation and degradation of thermogenic liquid hydrocarbons placed with the waste; or,
- thermal mechanisms such as thermal cracking or kerogens (see below).

These gases could also be involved in hydrogen generation, with hydrogen potentially generated by partial oxidation of propane in the presence of metal catalysts, similar to fuel cells. In the oil industry, much effort has focussed on 'wet gas' (propane, ethane, butane) production from kerogen. At temperatures below approximately 140° C, the gas wetness ratio is largely due to gases derived from kerogen cracking (excluding bacterial alteration). Thermogenic gas produced by thermal cracking of sedimentary organic matter into hydrocarbon liquids and gas can contain significant concentrations of "wet gas" components (ethane, propane, butanes) and condensate (C₅₊ hydrocarbons). Biogenic gas is typically dry (low in ethane, propane and butane) except in situations where it has been in contact with thermogenic liquid hydrocarbons. Observations from this dataset include:

- The ratio of methane to these gases is typically a factor of 3 to 4 orders of magnitude.
- The MBT residues at Site 5 represent the closest waste to typical MSW. The lack of 'wet' gases is noticeable in this waste.
- Site 7-2 has wet gases but no methane, suggesting their generation may not be linked to standard biodegradation mechanisms.
- The older European sites (4a, 4b and 4c) contain little of these gases. However, propane is regularly detected at relatively low concentrations, even in the absence of ethane and butane.

3.2.2 Hydrogen sulphide

Hydrogen sulphide was low or absent in gas at low carbon landfills. There is a potential relationship between hydrogen and hydrogen sulphide in the presence of metal. Iron corrodes in the presence of hydrogen sulphide to release hydrogen. The overall corrosion reaction is:



The ferrous ions either form iron sulphide phases or pass into bulk solution. The removal of hydrogen sulphide from the gas phase by partitioning into water and subsequent reaction with dissolved iron offers a route for its removal from low carbon landfill gas. Consequently, metallic iron and steel can act as chemical 'sinks' for hydrogen sulphide under both acidic and alkaline conditions.

3.2.3 Organic trace components

With the exception of Site 1, organic trace compounds were generally absent or present at concentrations orders of magnitude lower than would be present in co-disposed waste. No organo-sulphur compounds were detected in general except from MBT waste and sorted MSW waste not suitable for incineration. This is shown in Figure 2.

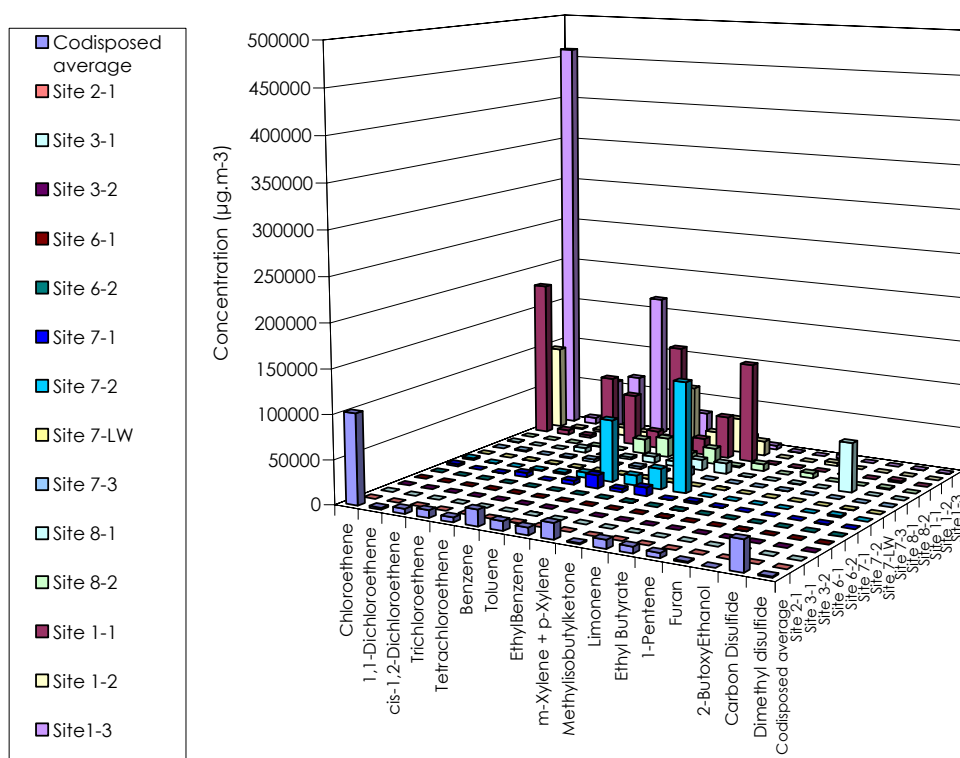


Figure 2. Organic trace component concentration in low carbon waste compared to the UK co-disposal average

Sites with interesting organic trace component signatures (apart from Site 1) were:

- Site 4A – there are freons in the fragmentiser waste, 8 years after emplacement. Dichloroethanes and chloroethane are also present at concentrations similar to 1-pentene.
- Gas from site 4B (waste not suitable for incineration) contains 1-pentene and carbon disulphide.
- Site 5 appears to be in a fermentative state of degradation, judging by the bulk gas data. The MBT process has not eliminated the Freon compounds, and has not used up all sources of sulphur, judging by the presence of carbon disulphide and dimethyldisulphide.
- Isolated sites contained relatively high methyl isobutyl ketone (Sites 1 and 7), 1-pentene (Sites 1 and 8), 1-butoxyethanol (Site 8) concentrations, obviously from specific waste streams. However, most sites had relatively low concentrations of these compounds.

Siloxanes are not likely to be produced in the landfill and are most likely emplaced during waste deposition. They have been detected in gas from recent waste (Site 1 and Site 5) and in waste placed 8 years ago (Sites 4A and 4C), suggesting that they are persistent.

3.2.4 Inorganic trace components

This project suggests that ammonia and amines do not constitute a large component of the gas from low organic content waste landfills.

Phosphine concentrations of 3 to 32 $\mu\text{g m}^{-3}$ (as phosphorus) have been measured in landfill gas at the Hooge Maey landfill in Flanders, Belgium (Roels and Verstraete, 2004). During this research, phosphine (as phosphorous) was detected at trace concentrations (20-30 $\mu\text{g.m}^{-3}$) at Site

1-1 and at trace concentrations ($30 - 40 \mu\text{g.m}^{-3}$) at Site 4a. Phosphine was not detected above the detection limit of $15 \mu\text{g.m}^{-3}$ at Points 6-1, 6-2, 7-1, 7-2, 8-1, and 8-2. The highest concentration of $50 \mu\text{g.m}^{-3}$ was measured in the leachate well at Site 7.

3.2.5 Organo-metal trace components

Organo-metal concentrations are shown in Table 3.1. Antimony and arsenic are generally detected in trace ($\sim 1 \mu\text{g.m}^{-3}$) concentrations. The average concentration of arsenic found in the gas from MSW landfill during two previous projects (Environment Agency 2002, 2003) was $51 \mu\text{g.m}^{-3}$. The lower concentrations in low carbon content landfills suggests that there is either less arsenic associated with the lower carbon waste, or potentially the lack of a carrier gas or lower temperatures mean that arsenic compounds are not as mobile. Selenium and tin are detected at trace concentrations approximately 50% of the time. Germanium and molybdenum are detected at trace concentrations less than 50% of the time. Tungsten is never detected. Tellurium is detected once at site 1, bismuth once at site 7.

Of the 22 gas samples taken, the mercury data can be summarised:

- Organic Mercury Average $0.6109 \mu\text{g.m}^{-3}$ Maximum $2.4700 \mu\text{g.m}^{-3}$
- Inorganic mercury Average $0.0159 \mu\text{g.m}^{-3}$ Maximum $0.0300 \mu\text{g.m}^{-3}$

This is at or below typical co-disposed waste gas mercury concentrations. In this project, mercury was only detected in UK sites. In the sites with mixed waste including contaminated land and other residues, organic mercury was typically 2 – 4 times the inorganic mercury concentrations. In contrast, the APC waste with some contaminated soil, only inorganic mercury was detected (ng.m^{-3} average).

Table 3.1. Highest average organo metal concentration

	Antimony	Arsenic	Bismuth	Germanium	Lead	Total Mercury	Molybdenum	Nickel	Selenium	Tellurium	Tin	Tungsten
	$\mu\text{g.m}^{-3}$	$\mu\text{g.m}^{-3}$	$\mu\text{g.m}^{-3}$	$\mu\text{g.m}^{-3}$	$\mu\text{g.m}^{-3}$	$\mu\text{g.m}^{-3}$	$\mu\text{g.m}^{-3}$	$\mu\text{g.m}^{-3}$	$\mu\text{g.m}^{-3}$	$\mu\text{g.m}^{-3}$	$\mu\text{g.m}^{-3}$	$\mu\text{g.m}^{-3}$
Site 1-1	0.4	1.3	0	4.9	7.2	0.0055	0.6	8.2	17.3	0.48	3.8	0
Site 1-2	0.5	0.7	0	2.8	9.4	0.0044	0	4.4	1.4	0	0	0
Site 1-3	0.7	0.9	0	0.6	23.1	0.48	0.9	8.5	1.5	0.2	1.2	0.4
Site 1-LW	1.4	1.6	0.2	1.2	46.8	2.5	0.3	24.1	3.1	0.5	2.2	0
Site 2-1	0.2	0.3	0	0	11	0.0055	0	2	0	0	0	0
Site 3-1	0.8	0.2	0	0	9.8	0	0.7	25.8	1.9	0	1.9	0
Site 3-2	0.3	0.5	0	2.6	7.2	0.009	0	13.1	2	0	0	0
Site 4a-1	1	0.3	0	1	2.8	0	0	1.2	0	0	0	0
Site 4a-2	0.1	0.5	0	1.3	5.7	0	0	4.3	2.9	0	1.1	0
Site 4b-1	0.2	0.4	0	0	60.2	0	0.4	4.4	0	0	0.7	0
Site 4c-1	0.1	0.3	0	0	15.1	0	0	4.4	0	0	0	0
Site 4c-2	1.5	1.1	0	0	42.7	0	0	4.2	0.7	0	0	0
Site 5-1	0.6	0.3	0	0	35.6	0	0	12	3.4	0	1.5	0
Site 5-2	0.4	0.9	0	0	20.6	0	0	20.6	0.5	0	1.2	0
Site 6-1	0.6	0.4	0	2.1	3.4	1.07	0	2.1	0	0	0	0
Site 6-2	0.5	0.2	0	3.9	1.1	0.33	0.4	1.1	19.4	0	0	0
Site 7-1	0.7	0.9	7.4	19.3	0	0.54	5.9	3.8	3.8	0	0	0
Site 7-2	0.3	0.5	0	1.6	12.4	0.29	0	2.1	1	0	0	0
Site 8-1	0.2	0.8	0	1.8	14.3	1.21	0	1.5	0	0	2.2	0
Site 8-2	0.4	1	0	2	46.8	0.13	0	2.4	1.1	0	7	0
Site 8-1	0.2	0.8	0	1.8	14.3	1.21	0	1.5	0	0	2.2	0
Site 8-2	0.4	1	0	2	46.8	0.13	0	2.4	1.1	0	7	0

4. IMPLICATIONS

4.1 Limitations on gas generation

Based on these data, the availability of water or a carbon source, or the build up of toxic compounds limits anaerobic gas generation. Thus, oxygen consuming chemical/biological reactions occur immediately after the waste is placed, but factors required for anaerobic degradation become exhausted, perhaps because of limited permeability in this waste. In this scenario, after an initial burst of activity the pore space is filled with quiescent material with a large potential for activity in the future when the landfill structure breaks down or when gas management or monitoring infrastructure is installed.

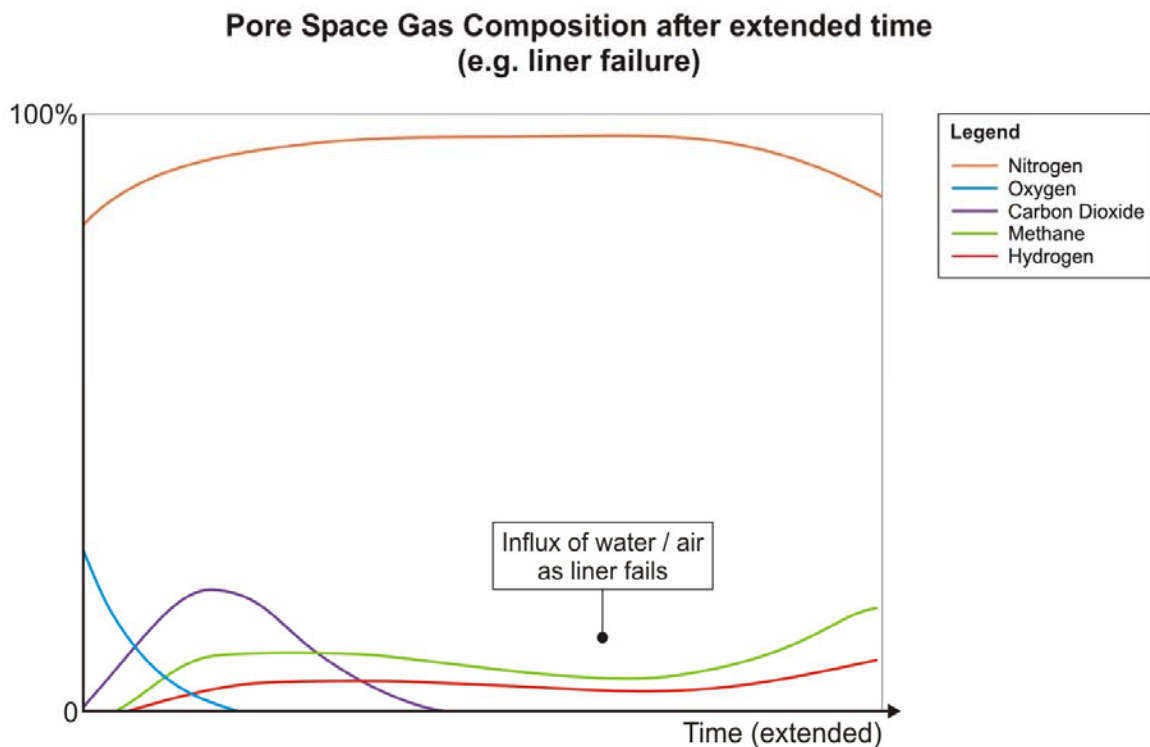


Figure 3. Low carbon hazardous waste landfill that restarts gas generation in the future

4.2 Revised conceptual model

Factors that limit gas generation within the waste mass are potentially absent in leachate wells and other penetrations into the waste. Leachate may transfer biodegradable material such as dissolved organic carbon and energy sources into an area of higher permeability and moisture. Biogenic methane generation is therefore more likely in the leachate control system of these landfills and can lead to a two system conceptual model – very limited gas generation within the waste mass and increased gas generation within the leachate management infrastructure.

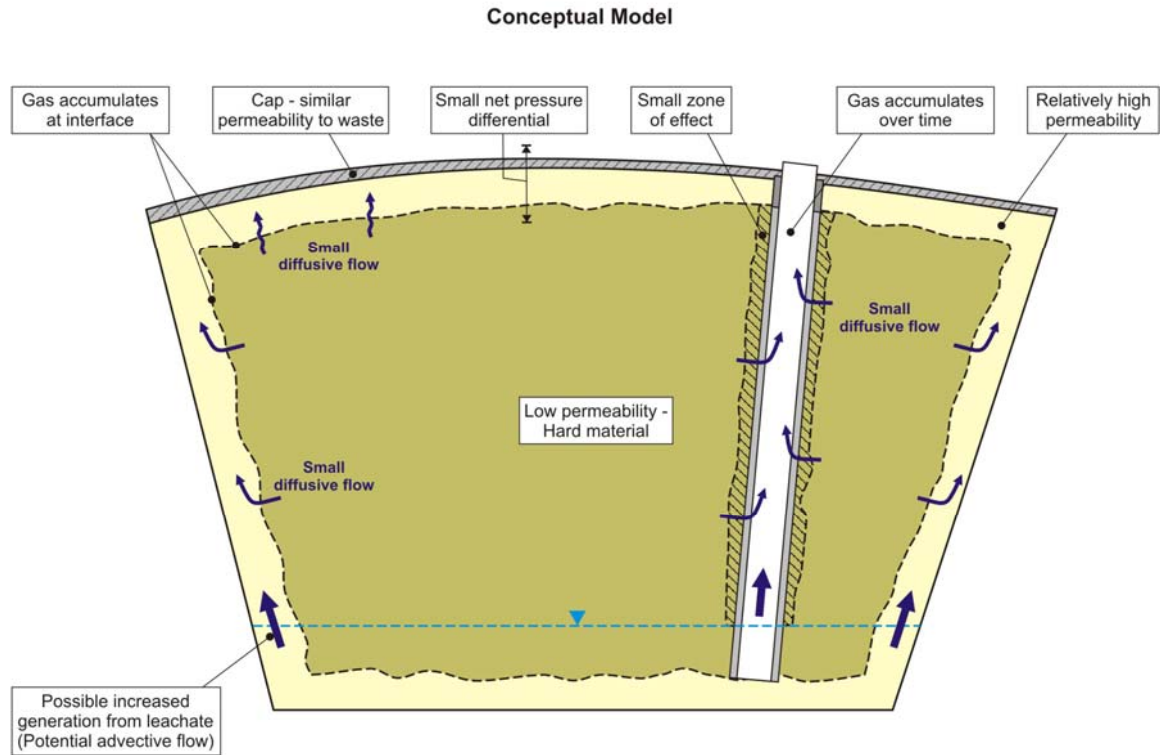


Figure 4. Two system conceptual model

4.3 Implications on monitoring

Gas sampling from monitoring wells or even monitoring arrays at low-carbon waste sites may be unrepresentative of the gas in the whole site for two reasons: 1) The low permeability of the waste and the resulting low flow of gas will mean the well or array will be representative of gas within close proximity to the well only, particularly when large volumes of gas must be sampled; and, 2) Gas generation is more likely close to penetrations into the landfill where permeability allows moisture (and potentially oxygen) to move into the waste. The higher rate of methane generation in these spaces may dilute the toxic trace gas concentrations in any emissions.

The data suggest that low carbon sites are spatially more heterogeneous than a similar MSW site and so predicting both short term variability and long-term equilibrium rates of gas generation is more difficult. New gas management and monitoring techniques at such sites should reflect the different conceptual model. One suggested method of sampling emissions from a low-carbon waste mass would be from a permeable blanket above the waste and below the cap. If this is not possible, several shallow, temporary installations may be sufficiently representative for risk assessment. Temporary installations benefit from not creating a permanent pathway for air and moisture potentially to enter the landfill and so are less likely to contribute to an increased risk of uncontrolled release of gas from the site.

4.4 Health and Safety Implications

The biodegradable carbon fraction in the waste is likely to contain a relatively larger proportion of petroleum and chlorinated compounds than typical MSW. 'Burst release' from landfill penetrations may occur when monitoring or leachate well caps are removed. This is potentially a Health and Safety issue because high concentrations of trace gases can build up in low-carbon landfills as a result of the absence of diluting bulk gases.

5. CONCLUSIONS

Oxygen from air and gas generated from waste appear to be removed into either a liquid or a solid phase material in the waste. In many low carbon/inorganic waste sites this results in the pore gas having a nitrogen concentration higher than atmospheric. Nitrogen gas enrichment can mean either negative pressure within the landfill, or slow air ingress into the landfill. Both these situations make it unlikely that there will be an overall gas emission from the landfill. Of the gases present in the resultant pore space, carbon dioxide is the gas that appears to be removed most easily, or is not generated, while methane and hydrogen are typically detected.

It is suggested that the availability of water or carbon, or the build up of toxic compounds currently limits anaerobic gas generation in low carbon landfill. If the previous postulation is correct, the emplaced 'quiescent' inorganic waste retains a potential for active gas production in the future when the landfill structure breaks down.

Gaseous compounds of lead and nickel are the most likely organo-metallic compounds to be found, though these are at very low concentrations. Organic trace components may be present and in some circumstances can be higher than in co-disposed waste due to the lack of diluting bulk gases.

Standard gas generation risk assessment models are not suitable for assessing emissions from low carbon landfills. The lack of gas pressure and permeability within these landfills means that there is unlikely to be a continuous gas migration pathway from the landfill. However, advective flow or burst release of gas is possible from permanent installations or up the high permeability side walls. Gas generation is more likely in leachate management infrastructure where moisture and high permeability are present.

ACKNOWLEDGEMENTS

UK and European site operators who allowed access to the sites for sampling. The Danish sampling would not have been possible without the help and assistance of Professor Charlotte Scheutz of the Danish Technical Institute. The German sampling was made possible with the help of Professor Rainer Stegman of the University of Hamburg.

REFERENCES

- ENVIRONMENT AGENCY, 2002. Investigation of the Composition and Emissions of Trace Components in Landfill Gas. R&D Technical Report P1-438/TR, Environment Agency, Bristol.
- ENVIRONMENT AGENCY, 2003. Quantification of Trace Components in Landfill Gas. R&D Technical Report/P1-491/TR, Environment Agency, Bristol.
- NAISH, C.C., BLACKWOOD, D.J., et al., 2001. The Anaerobic Corrosion of Carbon Steel and Stainless Steel. AEA Technology Report AEAT/R/ENV/0224, Harwell.
- ROELS, J. and VERSTRAETE, W., 2004. Occurrence and Origin of Phosphine in Landfill Gas. *Sci. Total Environ.*, 327, pp 185-196.