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Potential gas production from landfilling of inorganic wastes

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Steve Killeen

Head of Science

Executive summary

The Landfill Directive (1999/31/EC), brought into force in England and Wales as the Landfill (England and Wales) Regulations 2002, has begun to change the way the UK handles waste. It sets out three classes of waste landfill – inert waste, non-hazardous waste and hazardous waste.

As the UK seeks to meet the requirements of the Landfill Directive, a substantial proportion of biodegradable waste will be diverted away from landfill. This will increase the amount of secondary wastes containing a high proportion of inorganic material going to landfill. Gaseous emissions from landfills in the future will be much smaller in volume compared with existing landfills and will have a very different composition. This may have implications for the management, risk assessment and monitoring of landfill gas. This desk study is the first phase of a programme to better identify and quantify the gases arising from landfilling of waste streams containing a high proportion of inorganic material.

The likely composition of these waste streams was estimated to identify the potential reactions that could occur in current and future wastes. The range, type and relative quantities of any wastes accepted into landfill sites will vary between landfills, depending on the permit conditions and local waste producers. There is no agreed ‘typical waste’ for the future sites containing mainly inorganic wastes and so, for the purposes of this project, national waste data have been used to create model landfills from which to consider potential gas generation. Conceptual model inventories were generated for three categories of landfill site – hazardous, non-hazardous and inert. In addition, monofilled cells within a non-hazardous site were considered based on asbestos or gypsum wastes as the waste stream. Finally, monofilled cells containing air pollution control (APC) residues were considered for a hazardous waste site.

The evolution of chemical conditions within a landfill was then assessed. There will be a heterogeneous distribution of waste types within the landfill and, the more diverse the types of waste, the longer it may take for conditions to approach what could be described as near steady-state or equilibrium.

The presence of a continuous aqueous medium throughout a landfill cannot be assumed. Although the waste may be damp, saturated conditions may exist only at the base of the landfill or in regions of the waste above impermeable waste deposits. The dryer the landfill, the slower will be the rate of the general chemical reactions that are expected to occur.

These types of landfill will contain small amounts of putrescible materials and many of the wastes may create hostile local environments. This will restrict microbial action compared with a municipal solid waste (MSW) landfill today. However, soil and dusts containing microorganisms will be blown into the site and carried on some wastes. The general picture of microbial action in these landfills is one of activity where conditions are most favourable; these favourable environments will probably increase as the system evolves over time. In addition, the microbial populations will be adapting to the imposed conditions. However, the timescale for this and the rates at which microbial processes will occur are uncertain.

Most research on the generation of landfill gas has focused on understanding gas production from landfills containing a high proportion of putrescible materials, the consequent need to manage this gas and, if possible, to utilise the methane component. In these circumstances, microbial respiration and the biodegradation of organic materials to produce methane and carbon dioxide dominate gas evolution. There has been almost no investigation of gas generation from sites containing little or

no degradable organic material. Chemical reactions, rather than microbial action, are likely to be important factors in the generation of bulk gas under these conditions.

The main reactions that may generate gaseous products in a landfill with a high proportion of inorganic wastes can be considered in three main classes:

- chemical reactions that result in hydrogen formation (mainly corrosion of Fe, Al, Zn);
- other chemical reactions that could generate gaseous species (mainly reactions of carbides, reactions with acids, formation of metal hydrides and possibly metal carbonyls);
- microbial gas generation in environments with low proportions of organic material (ammonia, hydrogen sulphide, hydrogen, carbon dioxide, methane, alkylated metal(loid)s, phosphine).

The bulk gases produced from inorganic landfills (hydrogen, carbon dioxide, methane) are potentially the same as those from existing MSW landfills. However, the quantities of gas produced and their rates of production are likely to be different from MSW landfills due to the different waste inventories and, consequently, different chemical conditions and microbial environments.

Trace gases arise from chemical or microbial reactions though, in some cases, the mechanism of production is not known. They can be conveniently grouped into three classes:

- **Generated by chemical reaction**: H_2S (from sulphides), H_2Se, HSCN, HCN, SbH_3, AsH_3, simple hydrocarbons (from carbides), HCl etc., Hg, NH_3, N_yO_x, PH_3, H_2Se, $COCl_2$ (and potentially, under some circumstances I_2, Br_2, Cl_2, F_2, SO_2)
- **Generated by microbial action:** H_2S (from sulphate), R_2S, SbH_3, SbR_3, AsH_3, AsR_3, BiR_3, CO, CS_2, COS (and possibly the selenium analogues CSe_2 and COSe), simple hydrocarbons, organic acids, PbR_4, Hg, HgR_2, NH_3, N_yO_x, PH_3, H_2Se, R_2Se, R_2Te, SnR_4 (R = alkyl groups including methyl and, in this context only, partially substituted with R = H in some cases) and, potentially, alkylated species of other metals.
- **Generation mechanism uncertain** (possibly combination of microbial and chemical): $Ni(CO)_4$, $W(CO)_6$, $Mo(CO)_6$ and, possibly, other transition metal carbonyls.

Several of these gases (e.g. mercury, carbon disulphide) may also occur as 'as-disposed' contaminants in wastes. Organic compounds such as solvents, which are present in the waste as deposited, will be volatilised and will appear as trace components in the gas.

Calculations were performed to investigate the effect of metal corrosion on the evolution of the redox conditions of a landfill facility and the potential for hydrogen gas production. Calculations were performed for:

- an unsaturated landfill facility filled with waste and initially aerobic;
- a saturated landfill facility filled with waste and initially aerobic.

These calculations showed that it could take about 160 days for anaerobic conditions to be established in a capped landfill containing the model mixed hazardous waste under unsaturated conditions. This is the result of bare metal corrosion. The rate of corrosion, and thus the onset of anaerobic conditions, depends on the surface area of mild steel present. However, the results of the calculations are sensitive to the assumed gas migration properties of the landfill cap. Calculations for a water-saturated landfill show conditions could become anaerobic more rapidly, even at shallow depths.

Analytical methods of sufficient sensitivity exist for all the species likely to be of interest in gas emissions from future landfills. Portable monitors offer some possibilities for monitoring species such as hydrogen at levels of interest. However, they may not be sensitive enough to measure the concentration of some other trace species. 'Hyphenated' laboratory analytical techniques (e.g. GC-ICP-MS)* coupled with cryogenic trapping and focusing appear capable of analysing a range of volatile trace species at very low concentrations.

Potential methods for treating gas from future landfills are outlined. The two most likely methods for treating gas from future landfills appear to be either controlled combustion or scrubbing. However, existing designs of landfill gas flares are not likely to be adequate for the first of these and scrubbing techniques may generate significant secondary wastes.

The study has identified the need for:

- better characterisation of the waste inputs to landfills;
- gas data from the monitoring of sites known to have taken wastes typical of those expected to be landfilled in the future.

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* gas chromatography-inductively coupled plasma-mass spectrometry

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1 Introduction

This desk study is the first phase of a programme to better identify and quantify the gases arising from landfilling of waste streams containing a high proportion of inorganic material. The study aimed to:

- provide a scientific framework for assessing what gases may be produced;
- survey a selection of the published literature;
- review any relevant experience on dealing with gaseous emissions from various types of inorganic waste.

The overall objective of the work described in this report is to identify those gases that might be produced by landfilled inorganic waste. Specific objectives are to:

- understand what wastes might generate gas, the chemistry of the processes that generate the gas, and the methods that can be used to monitor and treat the gas;
- identify gaps in the data that might be relevant to gas production from wastes to be landfilled in the UK.

The study consists of six tasks:

1. Specify potential waste inputs and resulting environments
2. Review the chemistry of gas production
3. Identify all potential volatile products
4. Review the technical literature on gases from inorganic waste
5. Identify potential methods for monitoring gaseous products
6. Identify potential methods for treating the off-gases from inorganic waste.

This report describes work carried out on the six tasks. The legislative framework governing landfill operation is outlined in Section 2 and estimates of the composition of potential waste streams are derived in Section 3. The chemical and microbially mediated processes that may be involved are reviewed in Section 4 and this information is used in Section 5 to assess likely volatile products from inorganic wastes. Section 6 estimates whether conditions in landfills with predominantly inorganic wastes might be generally anaerobic or aerobic through metal corrosion. Section 7 discusses possible methods for monitoring and identifying gaseous products and Section 8 reviews methods that may be applicable to treating off gases with relatively low methane content. Section 9 summarises the report and draws conclusions.

2 Legislation and landfill operation

2.1 Site management and design

The Landfill Directive (1999/31/EC) has begun to change the way the UK handles waste. The Directive was brought into force in England and Wales on 15 June 2002 as the Landfill (England and Wales) Regulations 2002. It is being implemented on a gradual basis as allowed by the legislation.

Article 4 of the Landfill Directive sets out three classes of landfill (Envirowise 2005):

- landfill for inert waste;
- landfill for non-hazardous waste;
- landfill for hazardous waste.

Hazardous waste is controlled in the European Union under:

- EU Hazardous Waste Directive (Council Directive 91/689/EC) (Environment Agency 2003a);
- European Waste Catalogue (EWC) (2000/532/EC as amended by Decisions 2001/118/EC, 2001/119/EC and 2001/573/EC) (CEU 2002).

Non-hazardous waste is waste that is not defined as hazardous. Inert waste is a subset of non-hazardous waste that does not undergo significant chemical or biological reactions and does not pose a risk of pollution to the environment.

The acceptance of wastes at sites for inert and hazardous wastes are controlled by specific Waste Acceptance Criteria (WAC), which introduce rigorous waste pre-treatment requirements.

Annex I of the Landfill Directive lays down general requirements for all types of landfilling and covers (Envirowise 2005):

- choice of location with respect to population, geology, hydrogeology, and ecology;
- water ingress and leachate management;
- use of geological and /or synthetic liners (and top liners following closure) for protection of soil and groundwater. Permeability and thickness criteria are set for each class of landfill (Table 2.1).

Generally, the landfill must also have an effective leachate collection system and landfills receiving biodegradable waste must have a collection system for landfill gas – this being either used to produce energy or flared (Envirowise 2005).

The Landfill Directive is implemented in England and Wales through a Pollution Prevention and Control (PPC) permit scheme. Operators wishing to construct and operate any of the three main types of site – or a cell for stable non-reactive hazardous waste (SNRHW) within a non-hazardous site – must show through risk assessments how they propose to achieve the required standards for the type of site proposed.

Table 2.1 Lining requirements for landfills[1]

Landfill type	Primary (sealing) liner	Attenuation layer (geological barrier)	
		Thickness (m)	Hydraulic permeability[2] (m s^{-1})
Inert	Not required	≥1	$\geq 1 \times 10^{-7}$
Non-hazardous	Required	≥1	$\geq 1 \times 10^{-9}$
Hazardous	Required	≥5	$\geq 1 \times 10^{-9}$

Notes: [1] Environment Agency (2004a)
[2] Colloquial use – strictly hydraulic conductivity

2.2 Landfill gas

2.2.1 Gas management

The management of landfill gas at permitted landfills is covered primarily by the Landfill Directive. The overall aim of the Landfill Directive as expressed in Article 1:

> 'by way of stringent operational and technical requirements on the waste and landfills, to provide for measures, procedures and guidance to prevent or reduce as far as possible negative effects on the environment, in particular the pollution of surface water, groundwater, soil and air, and on the global environment, including the greenhouse effect, as well as any resulting risk to human health from landfilling of waste, during the whole lifecycle of the landfill'.[1]

Item 16 of the preamble to the Landfill Directive intimates that measures should be taken to reduce the production of methane and to control the landfill gas. This will, in part, be achieved by:

- reducing the amount of biodegradable municipal waste (BMW) disposed of to landfill;
- banning the deposit of certain wastes in landfills;
- pre-treating most wastes before their disposal to landfill.

Implementation of the Landfill Directive will result in a reduction of the volume of gas generated from waste. Changes in the waste composition may also result in a significant change in the composition of landfill gas.

Appropriate measures must be taken to control the accumulation and migration of landfill gas in all forms of landfill site. Landfill gas must be collected from all landfills receiving biodegradable waste and the landfill gas must be treated and, where possible, utilised. Landfill gas must be collected, treated and used in a manner that minimises damage to, or deterioration of, the environment and risk to human health.

2.2.2 Gas composition

The Landfill Directive defines landfill gas as: 'all the gases generated from landfilled waste'.

Based on this definition, landfill gas includes:

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[1] See http://ec.europa.eu/environment/waste/landfill_index.htm

- compounds generated by the biodegradation of waste;
- compounds arising from chemical reactions;
- gases due to the volatilisation of chemicals from the waste.

Methane and carbon dioxide from the biodegradation of organic wastes are the principal gases produced by most current landfills in the UK. Typical proportions of the bulk compounds in landfill gas are given in Table 2.2.

Table 2.2 Typical range of bulk compounds in landfill gas[1]

Bulk landfill gas	Typical value (%v/v)	Observed maximum (%v/v)
Methane	63.8	88.0
Carbon dioxide	33.6	89.3
Oxygen	0.16	20.9[2]
Nitrogen	2.4	87.0[2]
Hydrogen	0.05	21.1
Water vapour (typical %w/w 25°C)	1.8	4.0

Notes:
[1] Environment Agency (2004a)
[2] Close to the composition of air

Trace gases make up approximately 1 per cent by volume of typical landfill gas. These trace components arise from processes such as:

- the volatilisation of organic solvents in the waste;
- biodegradation of certain components of the waste to produce hydrogen sulphide or chloroethene (vinyl chloride);
- the corrosion of metals or reduction of inorganic components.

In landfill gas from municipal solid waste (MSW) landfills, the trace components are mixed within the bulk gas phase.

The following issues are of concern when considering minor components of landfill gas (Environment Agency 2002a):

- strong and often unpleasant odour that taints the landfill gas emission;
- contribution to the unpleasant character of condensate from gas lines;
- direct chemical attack on components in the gas management systems;
- generation of corrosive compounds on combustion as part of gas utilisation or management;
- potential harm to health from inhalation of particular compounds in gas;
- generation of potentially harmful substances on incomplete combustion during gas utilisation or management;
- unusually strong impact as a greenhouse gas;
- unusually strong impact on ozone depletion.

Organic substances constitute the greatest variety of trace components in current landfill gas, but some organometallic compounds may be significant. Several inorganic compounds, notably hydrogen sulphide (H_2S) and water, are common trace components (Environment Agency 2002a). The trace components originate from a number of sources (Table 2.3).

Table 2.3 Example sources of trace components in landfill gas

Type of source	Examples
Direct sources	• Out-gassing of waste • Vaporisation of low boiling point liquids such as volatile organic compounds (VOCs) in the waste • Anaerobic respiration by microorganisms • Corrosion of metals • Chemical reactions between organic or inorganic substances • Microbial degradation of organic substances
Indirect sources	• Equilibration of substances from the aqueous phase into the gas phase • Gas stripping of substances from leachate as a result of forced flow through the liquid • Aerosols carrying liquid phase • Dusts carrying material adsorbed on the solid

Approximately 500 trace compounds have been identified in landfill gas (Environment Agency 2002a). Scott *et al.* (1988) divided the composition of trace landfill gas into 12 generic groups:

hydrogen sulphide;

- alkanes (other than methane);
- alkenes;
- cyclic organic compounds (including aromatic compounds);
- halogenated compounds;
- alcohols;
- esters;
- carboxylic acids;
- amines;
- ethers;
- organosulphur compounds;
- other oxygenated compounds (principally ketones and furan derivatives).

2.2.3 Changes in landfill gas

Under the Landfill Directive a substantial proportion of biodegradable waste will be diverted away from landfill. There will be an increase in the disposal of secondary wastes containing a high proportion of inorganic material. These will include incinerator residues and reject materials from other waste sorting or treatment activities. The result will be that;

- the volume of gaseous emissions from landfills in the future will be much smaller;
- the gas will have a different composition compared with existing landfills.

The changes in composition and combustibility of the landfill gas will require more detailed consideration of the hazards from emissions previously disregarded as insignificant trace components.

Sites for waste with low organic contents will require revised landfill gas management practices and the assessments of the risk from gas will be different. In particular, the monitoring needs will be unlike those of a site taking biodegradable wastes.

Thus, there is a need to understand:

- which gases may be produced from the landfilling of waste streams containing high proportions of inorganic materials;
- how these gases may be treated.

3 Potential waste inputs and resulting environments

3.1 Inputs to different types of landfill

Article 6 of the Landfill Directive specifies the waste types that can be assigned to the three classes of landfill (Envirowise 2005).

- Only hazardous waste that fulfils the criteria set out in accordance with Annex II of the Landfill Directive can be assigned to a hazardous landfill.
- Inert waste landfill sites can only be used for inert waste (as defined in Article 2).
- Landfill for non-hazardous waste may be used for:
    - municipal waste;
    - non-hazardous waste complying with the acceptance criteria given in Annex II of the Landfill Directive;
    - stable, non-reactive hazardous wastes complying with the same acceptance criteria. These hazardous wastes cannot be deposited in cells for biodegradable, non-hazardous waste.

3.2 Waste inputs

In order to identify the reactions that could occur in current and future wastes, it is necessary to estimate the likely composition of the waste streams. The range, type and relative quantities of any wastes accepted into landfill sites will vary from one landfill to the next, depending on the permit conditions and local waste producers.

There is no agreed ‘typical waste’ for the future sites containing mainly inorganic wastes and so, for the purposes of this project, national waste data were taken to create model landfill inventories on which to investigate potential gas generation.

Conceptual inventories were generated for three categories of landfill site – hazardous, non-hazardous and inert. In addition, monofilled cells within a non-hazardous site were considered based on asbestos or gypsum wastes as the waste stream. Finally, monofilled cells containing air pollution control (APC) residues were considered for a hazardous waste site.

The methodology for estimating the model inventories for the mixed hazardous and mixed non-hazardous landfills uses data from the Environment Agency’s Hazardous Waste Interrogator (Environment Agency 2005a) and is given in Appendix A.

Table 3.1 gives the estimated composition of wastes that may be assigned to hazardous and non-hazardous waste landfills based on this methodology. However, these representative mixed waste inventories are based on an appreciable amount of expert judgement rather than detailed information on analyses of the various component waste steams. Although this is sufficient for this initial scoping exercise, these estimates should be reviewed as actual waste input information becomes available. In addition, if more waste is incinerated, this could have a significant impact on the composition of the residues going to landfill.

Table 3.1 Estimated annual notional model inventories for future mixed hazardous and mixed non-hazardous wastes disposed to landfill

Class of material	Mixed hazardous landfill		Mixed non-hazardous landfill	
	Total estimated mass (tonnes)	% of total by mass	Total estimated mass (tonnes)	% of total by mass
Iron and steel	1,230	1.1	7,920	5.4
Aluminium as metal	560	0.5	2,710	1.8
Zinc as metal	450	0.4	120	0.1
Cements and alkaline solids	160	0.1	19,600	13.3
Recalcitrant organic materials	750	0.6	17,400	11.8
Oils	5,270	4.6	350	0.3
Other non-halogenated organics and residues	1,220	1.1	13	0.0
Halogenated solvents and residues	1,430	1.2	11	0
Polyvinyl chloride (PVC)	11	0.0	1,060	0.7
Wood and paper	190	0.2	20,700	14.1
Other inorganic chemicals and other materials	66,300	57.5	12,600	8.6
Inert[1]	36,300	31.5	64,900	44.0
Lead	1380	1.2	23	0.0
Total (tonnes/year)	**115,251**	**100**	**147,407**	**100.1**

Notes: [1] Assumed inert in terms of ability to generate gas; not as defined by WAC.

3.2.1 Hazardous waste

Table 3.1 gives the model inventory for mixed hazardous waste disposed to landfill. In terms of percentage by weight, the composition is dominated by 'other inorganic chemicals and other materials' (58 per cent) and 'inert material'[2] (32 per cent). Together these account for approximately 90 per cent of the total landfilled hazardous waste.

Less abundant constituents include:

- oils (5 per cent);
- lead (1 per cent);
- iron and steel (1 per cent);
- halogenated solvents and residues (1 per cent);
- 'other' non-halogenated organic compounds and residues (1 per cent);
- recalcitrant organic materials (0.6 per cent);
- aluminium (0.5 per cent);
- zinc (0.4 per cent).

Paper, cardboard, etc. form only 0.2 per cent of the mass of the waste.

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[2] Inert in terms of gas generation potential, not in terms of the definition provided by Waste Acceptance Criteria

Although cements and alkaline solids only contribute 0.1 per cent of the total, it is possible that some wastes will be immobilised in cement and that this therefore is an underestimate.

3.2.2 Non-hazardous waste

Table 3.1 gives the model inventory for mixed non-hazardous waste disposed to landfill. In terms of percentage by weight, the largest category is 'inert material'[2] (44 per cent). Lesser contributions, in decreasing amounts, are provided by:

- wood and paper (14 per cent);
- cements and alkaline solids (13 per cent);
- recalcitrant organic materials (12 per cent);
- other inorganic chemicals and other materials (9 per cent);
- iron and steel as metal (5 per cent).

Together these six categories account for approximately 97 per cent of the total landfilled non-hazardous waste. Less abundant constituents include aluminium as metal (2 per cent) and PVC (0.7 per cent).

3.2.3 Inert waste

The types of waste acceptable in an inert waste landfill are given in Table 3.2. These can be broadly classified as:

- uncontaminated glass wastes from various sources;
- uncontaminated concrete, brick, tile and ceramics from construction and demolition (C&D);
- uncontaminated soil and stones from construction and demolition (C&D) sites, gardens and parks.

As most of these materials are inert (only low levels of plastics, metals, wood, rubber and other organic materials are permitted in these C&D wastes), no attempt was made to develop an approximate composition for these wastes if mixed in a landfill.

Table 3.3 gives the total amount of C&D wastes disposed to landfill in 2001 in England and Wales.

Table 3.2 Wastes acceptable in an inert landfill[1]

EWC code	Description	Other information
10 11 03	Waste glass-based fibrous materials from manufacture of glass and glass products	Only without organic binders
15 01 07	Glass packaging (including separately collected municipal packaging waste)	–
17 01 01	Concrete (C&D wastes)	Low content of plastics, metals, organic, wood, rubber etc.
17 01 02	Bricks (C&D wastes)	Low content of plastics, metals, organic, wood, rubber etc.
17 01 03	Tiles and ceramics (C&D wastes)	Low content of plastics, metals, organic, wood, rubber etc.
17 01 07	Mixtures of concrete, bricks, tiles and ceramics (C&D wastes)	Low content of plastics, metals, organic, wood, rubber etc.

EWC code	Description	Other information
17 02 02	Glass (C&D wastes)	Low content of plastics, metals, organic, wood, rubber etc.
17 05 04	Soil and stones (C&D wastes)	–
19 12 05	Glass from mechanical treatment (crushing etc.) not otherwise specified	–
20 01 02	Glass (separately collected fraction from MSW (excluding 15 01)	–
20 02 02	Soil and stones (garden and park wastes)	–

Notes: [1] Environment Agency (2002b)

Table 3.3 Estimates for England and Wales of C&D wastes sent to landfill, 2001[1]

Waste description	Total (tonnes)[2]
Clean, unmixed hard C&D waste disposed of at landfills	239,000
Mixed and/or contaminated hard C&D waste disposed of at landfills	394,000
Clean excavation waste disposed of at landfills	652,000
Mixed and/or contaminated excavation waste disposed of at landfills	1,318,000
Mixed construction, demolition and excavation waste (CDEW) and unspecified materials disposed of at landfills	1,619,000
Total	**4,222,000**

Notes: [1] Symonds Group (2005)
[2] These totals include contaminated waste that would be unsuitable for disposal at an inert landfill.

3.2.4 Monofilled wastes

Two model cells containing asbestos or gypsum (high sulphate) wastes were considered for a non-hazardous waste site and an APC residues monofill cell was generated for a hazardous waste site. Monofills were assumed to contain single or closely-related waste streams.

Asbestos wastes

Asbestos waste appears to be dominated by two waste streams from the construction and demolition industry. As described in the EWC, these are:

- 17 06 01 Insulation materials containing asbestos (M)[3] – 88,700 tonnes in 2001 (Symonds 2005);
- 17 06 05 Construction materials containing asbestos (M) – 297,400 tonnes in 2001 (Symonds 2005).

Waste stream 17 06 05 was assumed to be 17 per cent white asbestos with the remainder mostly being concrete (e.g. asbestos-cement sheet, etc.) although small amounts of glass, steel and wood are also likely to be present.

About 50 per cent of waste stream 17 06 01 was assumed to be fibrous asbestos insulation with the remainder being glass fibre. Plastic material used in bagging and containment will also be present.

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[3] See Appendix A of Technical Guidance WM2 (Environment Agency 2003a) for an explanation of absolute (A) and mirror (M) entries in the European Waste Catalogue.

In addition, some asbestos wastes could contain the residues of polyvinyl alcohol used in sprays to suppress dust during asbestos removal and may also include used items of clothing and safety equipment. Foams (e.g. urea formaldehyde-based materials) may also be present. These additional materials will make up a very variable proportion of the waste stream but are assumed here to be only a few percent of the total weight.

Gypsum wastes

Gypsum wastes were assumed to consist of plasterboard and similar products. In general, plasterboard consists of a core of calcium sulphate dihydrate encased in paper liners. Minor additives include starch, foaming agents and dispersants. Fibreboard is plasterboard with a glass fibre fleece. Moisture-resistant boards and core board contain a silicone additive. Fire-resistant boards and core board include small quantities of glass fibre and vermiculite. Foil-backed boards are backed with a metallised polyester film.

It was assumed that the waste consisted of:

- 97.4 per cent gypsum;
- 1 per cent paper;
- 1 per cent glass fibre;
- 0.1 per cent starch, foaming agents, dispersants, glass fibre, vermiculite;
- 0.5 per cent metallised polyester film.

The most appropriate EWC code for gypsum wastes arising from construction or demolition work is likely to be 17 09 04 (mixed construction and demolition wastes other than those mentioned in 17 09 01, 17 09 02 and 17 09 03). This is used most frequently as describing a mixed load from a typical construction site (SEPA 2004).

Where separate production and collection takes place such that the most appropriate waste code is 17 08 02 (gypsum-based construction materials other than those mentioned in 17 08 01), subsequent disposal will be required against the criteria of the Landfill Directive, i.e. to a separate cell (SEPA 2004).

The limit for the total organic carbon content of wastes landfilled together with gypsum-based materials is 5 per cent (SEPA 2004).

APC residues

APC residues are obtained from flue gas treatment at MSW incinerators (19 01 07, solid wastes from gas treatment (A) from incineration or pyrolysis of waste)

APC residues have a high alkalinity (pH 12) due to the unreacted lime content of the waste stream and consist of:

- large amounts of calcium, chlorides, sulphates, carbonates, sodium and potassium;
- fine fly ash particles;
- dioxins and furans;
- heavy metal salts.

Indicative metal concentrations are given in Table 3.4.

Some APC residues were landfilled directly either in dry bagged form or mixed with water. The latter washes out some of the free lime, reduces the alkalinity and exploits the pozzolanic properties of the material to solidify the material into a monolithic waste. There is ongoing research into the properties and treatment of APC residues as current methods failed to meet the requirements of the full WAC when these came into force in July 2005. One option is to mix with cement to solidify the waste and reduce the leachability of some of the components of the waste.

Table 3.5 shows some elemental concentrations in a sample of MSW incinerator bottom ash from Bavaria, Germany.

A study of the sustainable landfill concept for predominantly inorganic wastes in the Netherlands was reported at the Ninth Sardinia International Waste Management and Landfill Symposium (van der Sloot *et al.* 2003). The project is an initiative of Alvalzorg, Essent, VBM and Stainkoeln, and involves a combination of laboratory simulations, test waste lysimeters and a 12,000 m^3 demonstration cell of predominantly inorganic wastes. The project is concerned primarily with leachate quality and no measurement of landfill gas generation was reported. The species detected in the leachate from the test inorganic cell are summarised in Table 3.6.

Table 3.4 Indicative metal concentrations in air pollution control residues

Metal	**Concentration**[3]	**Units**
Study 1[1]		
Zn	6.2	$g\ kg^{-1}$
Pb	2.4	$g\ kg^{-1}$
Fe	1.7	$g\ kg^{-1}$
Mg	7.9	$g\ kg^{-1}$
Cu	550	$10^{-3}g\ kg^{-1}$
Mn	340	$10^{-3}g\ kg^{-1}$
Cr	100	$10^{-3}g\ kg^{-1}$
Cd	91	$10^{-3}g\ kg^{-1}$
Study 2[2]		
Cd	210	$10^{-3}g\ kg^{-1}$
Cu	2,500	$10^{-3}g\ kg^{-1}$
Mo	82	$10^{-3}g\ kg^{-1}$
Pb	3,000	$10^{-3}g\ kg^{-1}$
Sb	500	$10^{-3}g\ kg^{-1}$
Zn	4,500	$10^{-3}g\ kg^{-1}$
As	36	$10^{-3}g\ kg^{-1}$
Cr	1,200	$10^{-3}g\ kg^{-1}$

Notes:
[1] Ferreria *et al.* (2003)
[2] van der Sloot *et al.* (2001)
[3] Rounded to two significant figures

Table 3.5 Trace element concentrations in a sample of Bavarian MSWI bottom ash[1]

Element	Concentration[2] (10^{-3}g kg^{-1})
As	8.2
Cd	8.1
Co	15
Cr	180
Cu	2,800
Mn	1,400
Ni	130
Pb	1,100
Sb	53
Zn	3,600

Notes:
[1] Weigand *et al.* (2003)
[2] Rounded to two significant figures

Table 3.6 Leachate composition from 12,000 m^3 test cell of inorganic wastes at pilot demonstration project at Nauernasche Polder Landfill, Netherlands

Substance/parameter	mg kg^{-1}	Substance/parameter	mg kg^{-1}
pH	7.2	Hg	7.0×10^{-7}
As	0.13	Mo	0.12
Ba	0.5	Ni	0.14
Cd	0.02	Pb	0.35
Cl	3,300	Sulphate	12,000[2]
Cr	0.019	Sb	0.06
Cu	0.038	Se	0.05
DOC[3]	350	Zn	0.8

Notes:
[1] van der Sloot *et al.* (2003)
[2] Rounded to two significant figures
[3] DOC= dissolved organic carbon

3.3 Evolution of waste environments in landfills

3.3.1 General issues

A number of general issues arise when considering the evolution of conditions within the different types of landfill.

There will be a heterogeneous distribution of waste types within the landfill. This means that the chemical conditions in regions of the cells may be quite different for long periods of time.

Water will provide a reagent by which chemical reactions (e.g. hydrolysis) may occur and a reaction medium through which the chemical conditions within a cell begin to equilibrate. The more diverse the types of waste, the longer it may take for conditions to approach what could be described as near steady-state or equilibrium. Therefore, it is easier to consider the evolution of conditions within a monofilled cell than in a landfill containing mixed waste.

The presence of a continuous aqueous medium throughout a landfill cannot be assumed. Water is expected to enter a landfill from above as rainfall percolating through the surface or cap. Inert landfills need have no liner and so water may also enter through the base and the sides of the landfill. Some limited water ingress through the liner may occur at engineered landfill sites with hydraulic containment (hazardous and non-hazardous). If parts of the liner fail, water can also enter through the base and sides of these landfills, restricted only by the performance of the attenuation layer (Table 2.1).

During operation of the landfill, leachate would not generally be allowed to accumulate and would be drained via a suitable collection system and treated. Thus, although the waste may be damp, saturated conditions may exist only at the base of the landfill or in regions of the waste above impermeable waste deposits (perched water).

The amount of water saturation throughout the wastes and the degree of failure of any waste containment (e.g. metal drums, polythene drums, bottles and sacks) will determine how rapidly reactions occur within the waste body. The dryer the landfill, the slower will be the expected rate of the general chemical reactions, and thus the slower the evolution of uniform conditions for parameters such as pH, redox potential and leachate composition. The possible evolution of anaerobic conditions due to metal corrosion and the effect on gas generation from iron and steel are considered in more detail in Section 6.

After closure of the landfill but while management of the site continues, it is expected that leachate would continue to be collected and treated. At some point, however, this is likely to cease and it is possible that a landfill cell could eventually fill with leachate. This is made more probable since it is likely that the cap to the landfill would fail prior to significant failure of the containment provided by the engineered base and sides of a lined landfill. At some point, sufficient water would be present to allow conditions in the landfill to approach steady-state or equilibrium. However, this could be many years after closure of the site.

The small amounts of putrescible materials in the predominantly inorganic waste landfills mean that microbial action will be restricted. In addition, many of the wastes within mixed waste landfills would pose hostile local environments where microbial activity is unlikely. However, soil and dusts containing microorganisms will be blown into the site and carried on some wastes. These will create an inoculum for microbial growth in favourable locations. The general picture of microbial action in these landfills is one of activity where conditions are most favourable. These favourable environments will probably increase as the system evolves over time. The microbial populations will also adapt to the imposed conditions. The timescale for this and the rates at which microbial processes occur are currently uncertain.

3.3.2 Hazardous waste environment

The major class of materials in the model mixed hazardous waste inventory (Table 3.1) is ‘other inorganic chemicals and other materials’. It is not possible to conclude what the effect of these will be on the chemical conditions in the landfill as there is insufficient detail on the nature of these wastes.

The mixed hazardous waste inventory also contains a considerable amount of material that was assigned as inert waste (32 per cent) in terms of its ability to generate gas or influence the chemical conditions. This is considered not to influence the chemical conditions in the landfill.

Cements and alkaline solids form only 0.1 per cent of the total, but, as noted in Section 3.2.1, the use of cements to treat some wastes may be under-represented in the model inventory. Therefore, it is not possible to comment in detail on how the pH of the landfill may develop. As acids are excluded from landfill, it can be postulated that the presence of sufficient cements and alkaline solids would tend to drive the pH towards alkalinity in a well-mixed system. A better definition of the inventory in a landfill or cell would enable this to be addressed in more detail, although a fully-mixed system would still have to be assumed.

The presence of iron and steel (1 per cent), aluminium (0.5 per cent) and zinc (0.4 per cent) as metal means there is the potential to generate hydrogen through corrosion. This is discussed in more detail in Section 6.

The small amount of wood and paper (0.2 per cent) could result in the generation of carbon dioxide and methane by microorganisms. It is also possible that some of the non-halogenated organic wastes (1 per cent) may be degraded readily by microbial action. But widespread microbial activity may be hindered by chemical conditions if these are highly alkaline. The initial microbial inoculum would also be low compared with an existing MSW landfill.

Amounts of methane and carbon dioxide at four investigated landfills accepting demolition and 'difficult' wastes show methane concentrations of 0–30 per cent and carbon dioxide concentrations of 0–20 per cent (Westlake *et al.*1991), though there is no indication of the flux of these gases from the waste.

3.3.3 Non-hazardous waste environment

Key differences (Table 3.1) between the model non-hazardous waste inventory and the mixed hazardous waste inventory are the former's higher proportions of:

- wood and paper (14 per cent);
- cements and alkaline solids (13 per cent);
- recalcitrant organic material (12 per cent);
- iron and steel (5 per cent);
- aluminium (2 per cent).

The 'other inorganic chemicals and other materials content' is 9 per cent – much lower than the hazardous waste inventory. The inventory is dominated by inert material (44 per cent). There is more potential for bulk gas generation from the non-hazardous waste than from the hazardous waste due to its higher metal, wood and paper content.

It can be postulated that the presence of larger amount of cements and alkaline solids would tend to drive the pH towards alkalinity in a well-mixed system. But because of the uncertainty about the nature of many of the chemicals and other materials disposed of, it is possible that the alkaline buffering capacity of the cements may be consumed. A better definition of the inventory in a landfill or cell would enable this to be addressed in more detail, though a fully-mixed system would have to be assumed.

3.3.4 Inert waste environment

Conditions in parts of an inert waste landfill are expected to be alkaline (e.g. pH 12.5) due to the significant amounts of cement and concrete in the waste. Carbonation of the surfaces of cement and concrete may result in the evolution of a slightly less alkaline pH.

Hydrogen may be produced from the small amount of iron and steel present if conditions become anaerobic.

Where soil is landfilled, it will provide a microbial inoculum and small amounts of carbon dioxide (and methane if conditions become anaerobic) may be generated from any traces of wood and cellulosic materials that are also landfilled. Data given by Westlake *et al.* (1991) and cited by Williams (2005) show detectable amounts of methane and carbon dioxide in landfill gas at some of six investigated landfills accepting demolition and 'inert' wastes (Table 3.7).

No leachate analyses were reported for Sites 24, 25 and 26. However, leachate from Site 21 had a higher chemical oxygen demand (COD) and total organic carbon (TOC) concentration than Sites 22 or 23. Leachate from all the sites had a pH value of more than 7.0 (Westlake *et al.* 1991).

However, sites permitted for inert waste will exclude some of the more degradable materials that could have been placed in sites classified as inert under the Waste Management Licensing (WML) scheme. Hence gas generation from permitted sites should be extremely low.

Table 3.7 Proportions of methane and carbon dioxide in landfill gas from six sites accepting demolition and 'inert' wastes[1]

Site	Methane (%)	Carbon dioxide (%)
21	0	3
22	0	1
23	0	0
24	2	10
25	4	5
26	55	35

Notes: [1] Westlake *et al.* (1991)

3.3.5 Monofilled waste environments

Asbestos and gypsum wastes were considered as they are the two waste streams to be landfilled in separate cells in a non-hazardous landfill.

The presence of asbestos cement in asbestos wastes will lead to the development of an alkaline pH as discussed above for inert waste. Again there is the possibility of the generation of small amounts of hydrogen, carbon dioxide (and methane) from a cell containing these wastes due to traces of iron, steel and wood. However, the initial microbial inoculum will be much lower compared with inert waste as no waste soil should be placed in the cell.

Within gypsum waste, there is the potential for hydrogen sulphide production due to the activity of sulphate-reducing bacteria (SRB). This potential will be lessened by excluding other materials (e.g. putrescibles and other organic material) from the cell.

In addition, a separate cell in a non-hazardous waste landfill is required to be sufficiently self-contained. The following principles are applied (SEPA 2004):

- no physical contact with any other wastes except suitable inert wastes used as cover materials;
- the purpose of any engineered barriers is to separate physically the waste types;
- the design and location of the cell should minimise the need for leachate management within the cell;
- there should be limited, if any, contact of landfill gas and leachate from the biodegradable wastes with the gypsum wastes;
- the gypsum waste cell must not compromise the landfill gas and leachate management of the biodegradable waste cells.

However, it may be difficult to minimise the need for leachate management.

In addition, the waste cells will contain some organic material (e.g. paper liners on plasterboard) and it is probable that hydrogen sulphide will be generated from low levels of microbial activity. At some point in the future after the failure of the cell cap or liner, it is probable that organic material could enter the cell via surface water or groundwater. This could lead to the possibility of continued hydrogen sulphide production.

A monofilled cell containing untreated APC residues will have a high pH (~12) due to the presence of unreacted lime. Since July 2005, these wastes have had to be treated prior to landfilling. Although there should be no bulk degradable organic materials, dioxins and furans may be present in small quantities. The waste also contains sulphates and heavy metals.

It is probable that some of the waste would not develop chemically reducing conditions and microbial action would be restricted by the hostile, highly alkaline conditions. However, it would appear that there is the potential for slow evolution of trace gases from:

- microbial action in protected niches (e.g. H_2S from sulphate);
- products from any reactions with finely divided metals and salts;
- VOCs from the organic content of the residues.

Aluminium particles occur in incinerator bottom ash and fly ash and will corrode under alkaline conditions (see Section 4.1.2) to produce hydrogen (Mizutani *et al*. 2000, Magel *et al.* 2001).

Hydrogen generation in a Bavarian monofill for bottom ash and gas cleaning residues from a MSW incinerator has occurred since 1977, a year after opening, and is expected to continue for several decades (Magel *et al.* 2001). Samples of bottom ash contained 0.5–4.3 volume per cent total metal, similar to a cited total metal content of 2.1 weight per cent (1.1 weight per cent aluminium, 0.6 weight per cent copper and 0.4 weight per cent iron) in another study (Burg 1999, cited in Magel *et al.* 2001).

Peak temperatures of 87°C were measured within a German landfill for MSW incinerator ash three months after disposal (Klein *et al.* 2001) due to reactions occurring within the ash.

Mizutani *et al*. (2000) describe two accidents involving hydrogen generation from MSW incinerator ash. Their study found that the hydrogen generation potential of fly ash from fluidised bed incinerators was greater than from stoker incinerators and was correlated with reducing potential.

4 Potential gas production processes

Most research on the generation of gas from existing landfills has focused on wastes containing a high proportion of putrescible materials and the consequent need to manage the biogas they produce. In these circumstances, microbial respiration and the biodegradation of organic material to produce methane and carbon dioxide dominate gas evolution. Very limited investigation has been made of gas generation from sites containing little or no degradable organic material. Chemical reactions rather than microbial action are likely to be important factors in the generation of bulk gas under these conditions.

Gas generation processes in a landfill containing small amounts of degradable organic material may be similar to those that could occur in repositories for radioactive waste where putrescible organic materials are excluded. Substantial R&D programmes have been conducted in support of the assessments of various repository designs. Therefore, the understanding developed for such repositories (see, for example, Biddle *et al.* 1987), has some application to shallow landfills provided allowance is made for different chemical and physical environments.

Reports relating to the US Department of Energy Waste Isolation Pilot Plant (WIPP) (USDOE 2000) and the Yucca Mountain Geological Repository (USDOE 2002) consider non-radioactive emissions to air of nitrogen dioxide (NO_2), carbon monoxide (CO), particulate matter from vehicle and generator exhaust during repository operation. Consideration of gaseous emissions included small quantities of VOCs, which may accumulate in the headspace of the waste packages.

In general, the principal gases generated from radioactive wastes in underground repositories are judged to be (Rodwell *et al.* 1999, 2004):

- hydrogen (H_2) from the corrosion of metals;
- carbon dioxide (CO_2) and methane (CH_4) from the microbially mediated degradation of organic materials.

The production of other gases that might occur in trace quantities was also considered in these assessments. The most significant radioactive gases produced are tritiated hydrogen, and carbon-14 substituted methane and carbon dioxide; radioactive gaseous emissions from waste packages may also include radon-222 and radioactive noble gases (principally krypton-85).

As part of the Nirex research programme in the UK into options for the long-term management of intermediate-level and some low-level radioactive wastes, the generation of gas in a radioactive waste repository containing such wastes was considered (Biddle and Moreton 1995). In contrast to MSW landfills, putrescible wastes are excluded and the organic material consists mostly of cellulose-containing wastes (paper, cardboard, wood) and a range of synthetic polymers (PVC, polythene, etc). Much of this work focused on the bulk gases arising for the corrosion of metals (hydrogen) and from the microbial degradation of organic materials (methane, carbon dioxide) (Nirex 1997, Nirex 2001, Hoch and Rodwell 2003).

This work is particularly relevant to the issue of hydrogen production from landfilled wastes with a relatively low organic content that are in contact with alkaline materials (e.g. concrete and cements from C&D wastes) or wastes that are alkaline (e.g. APC residues, waste immobilised in cement).

Biddle *et al.* (1998) considered the post-closure evolution of minor active and toxic gases for a radioactive waste repository in the UK. Those identified are given in Table 4.1. They include gases whose most likely mode of generation was considered, in the context of that work, to be due to radiolysis (denoted by an R in the second column of Table 4.1), with hydrogen atoms and methyl and other organic radicals being important intermediates. Although radiolysis is not applicable to a landfill, these entries are retained for completeness (alternative routes for their production are identified in the discussion below).

Typical uses of a number of elements with potential volatile inorganic or organometallic (alkylated or carbonyl) compounds are given in Table 4.2. These examples show that all these elements are likely to be present in wastes disposed to mixed waste landfills.

The main reactions that might generate gaseous products in a landfill with a high proportion of inorganic wastes are considered in three main classes below.

- The chemical reactions that result in hydrogen formation are dealt with in Section 4.1.
- Other chemical reactions that could generate gas are considered in Section 4.2.
- Microbial gas generation in environments with low proportions of organic material are covered in Section 4.3.

Finally, substances that may be volatilised from deposited waste are summarised in Section 4.4.

Table 4.1 Minor toxic gases that might form in a radioactive waste repository[1]

Gas	Method of formation[2]	Reactive in repository?
CH_3X (X = halogen)	Mainly R (CH_4 or CH_3 + HX or X_2)	May be hydrolysed
$(CH_3)_2Se$	R (Se + CH_3)	May be hydrolysed
Cl_2	R	Very reactive
HCl	R and C (from organic waste)	Very reactive
HI	R and C (from organic waste)	Very reactive
SnH_4	R (Sn + H)	Unstable
PbH_4	R (Pb + H)	May not exist
SbH_3	R (Sb + H)	Unstable
BiH_3	R (Bi + H)	Unstable
$Ni(CO)_4$	C (Ni + CO)	Unstable
H_2Se	R (Se + H)	Forms metal selenides
H_2S	R (S+ H)	Forms metal sulphides
NH_3	R (reactions involving NH_4, NO_3 trapped N_2, N-containing polymers)	Stable but very soluble
I_2	R	Unstable (goes to iodide)
$HSeCH_3$ 3)	R (Se, H, CH_3)	Probably unstable
$HSCH_3$ 3)	R (S, H, CH_3)	Probably reactive
$MeSnH_3$ 4)	R (Sn, H, CH_3)	Probably reactive
$MePbH_3$ 4)	R (Pb, H, CH_3)	Probably reactive
CO	R and M (organics)	Fairly reactive
Organic gases and vapours other than CH_4	R, C and M (organics)	Some are reactive

Notes:
[1] Adapted from Biddle *et al.* (1998).
[2] R = radiolytic; C = chemical; M = microbial.
[3] And similar compounds containing larger alkyl groups.
[4] And similar compounds containing additional and/or larger alkyl groups.

Table 4.2 Typical uses of elements with common volatile inorganic, alkylated or carbonyl compounds[1]

Element	Typical uses of the element and its compounds
Antimony	Semiconductors, lead alloys, batteries, anti-friction alloys, cable sheathing, paints, ceramics, glasses, pottery, medicine
Arsenic	Bronzing, pyrotechnics, doping agent for electronics industry
Bismuth	Malleable iron, acrylic catalyst, thermocouples, fire detection, cosmetics, medicine
Bromine	Fumigants, water purification, dyes, medicines, flame-proofing agents, photography
Chlorine	Water industry, paper production, dyestuffs, plastics, insecticides, cleaning products and many other consumer items, organic solvents
Fluorine	Chemicals and plastics, glass etching, refrigerants, toothpaste, water industry
Germanium	Electronics, alloys, fluorescent lamps, catalysts, infrared optics
Iodine	Medicine, photography, food industry
Lead	Batteries, plumbing, radiation shielding, roofing, old paints, glass
Mercury	Thermometers, barometers, diffusion pumps, batteries, lighting, caustic soda and chlorine production, dentistry, pesticides
Molybdenum	High-strength steels, electrodes in glass industry, aviation industry, catalysis, electrical filaments, lubricants (MoS_2)
Nickel	Stainless steel, nickel steel armour plate, glass production, nickel plating, catalysts, electroplating
Phosphorus	Safety matches, pyrotechnics, fertilizers, glass, steels, water softeners, pesticides
Selenium	Photovoltaics and photoconductors, rectifiers, semiconductors, photocopying, glass production, stainless steel
Silicon	Electronics, silicones, glass manufacture (silica), lubricants
Sulphur	Sulphuric acid, fertilisers, rubber vulcanisation, fungicides and fumigants, bleaching and preservative in food industry, paper production,
Tellurium	Semiconductors, alloys with cast iron, copper and stainless steel, lead additive, ceramic and glass
Tin	Metal coatings (tin cans), alloys (soft solder, pewter, bronze, etc.), electrically conductive coatings, float glass (molten tin), biocides
Tungsten	Electrical filaments, glass-metal seals, automobile contact points, X-ray targets, furnace windings, tool steels, tungsten carbide, fluorescent lighting, chemical and tanning industries, lubricant (WS_2), paints

Notes: [1] Data taken from WebElements™ Periodic Table (professional edition), copyright M. Winter, University of Sheffield, 1993–2006 (http://www.webelements.com).

4.1 Hydrogen production from metal corrosion

4.1.1 Iron and steel

The corrosion of iron and steel under alkaline or neutral conditions only leads to the generation of hydrogen under anaerobic conditions:

$3Fe + 4H_2O = Fe_3O_4 + 4H_2$

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

$Fe + 2H_2O = Fe(OH)_2 + H_2$, followed by

$3Fe(OH)_2 = Fe_3O_4 + 2H_2O + H_2$

Although Fe_3O_4 (magnetite) is the thermodynamically favoured end product, $Fe(OH)_2$ may be formed at temperatures below 60ºC as the conversion reaction to magnetite is inhibited.

Under aerobic conditions, corrosion of iron may be represented by:

$4Fe + 3O_2 = 2Fe_2O_3$; or

$4Fe + 6H_2O + 3O_2 = 4Fe(OH)_3$

As conditions evolve from aerobic to anaerobic, oxide film reduction occurs:

$4Fe_2O_3 + Fe = 3Fe_3O_4$

$2Fe(OH)_3 + 4Fe + 2H_2O = 2Fe_3O_4 + 5H_2$

Under acidic conditions, the corrosion of iron and steel produces hydrogen by the reaction:

$Fe + 2H^+ = Fe^{2+} + H_2$

The rates of corrosion reactions depend on:

- pH
- surface area
- temperature
- iron and steel composition.

The total amount of hydrogen produced depends on the amounts of iron and steel that corrode under anaerobic conditions. The rates and chemistry of steel corrosion under neutral and alkaline conditions are reviewed by Smart (2002).

4.1.2 Aluminium

Aluminium corrodes according to the equation:

$Al + 3H_2O = Al(OH)_3 + 1.5H_2$

The corrosion of aluminium at neutral pH values produces a protective corrosion film of aluminium oxide and aluminium hydroxide. This explains its resistance to corrosion despite the fact that aluminium is highly electropositive (Cotton *et al.* 1999). Aluminium oxide and hydroxide are amphoteric and dissolve under acidic or alkaline conditions, thereby exposing the aluminium surface to further corrosion and increasing the overall rate of corrosion.

The main constituent of the corrosion film at high rates of corrosion is aluminium hydroxide, although aluminium oxide may be formed at low rates of corrosion. The aluminium hydroxide film is porous and the rate of corrosion of the underlying metal surface depends on the thickness of the film. This is turn is determined by the pH and composition of the solution in contact with the metal. For example, the presence of calcium in solution leads to the formation of calcium aluminate in the corrosion film, which reduces the rate of corrosion. In contrast, dissolved sodium and potassium interact with the corrosion film so as to increase the rate of corrosion.

The rate of alkaline corrosion of aluminium particles in landfilled incinerator bottom ash is reduced by their inclusion in glass formed during combustion or by the formation of alteration products on the surface of aluminium particles (Magel *et al.* 2001). Although the presence of chloride in solution does not affect the general corrosion rate of aluminium in sodium, potassium or calcium hydroxide solutions, or in cementitious materials, it promotes galvanic coupling of aluminium in contact with iron and steel. This leads to an enhanced rate of aluminium corrosion, which is dependent on pH.

These reactions are not affected by redox conditions.

4.1.3 Zinc

Zinc reacts readily with non-oxidising acids releasing hydrogen (Cotton and Wilkinson 1980):

$Zn + 2H^{+} = Zn^{2+} + H_2$

Zinc also dissolves in strong bases to release hydrogen:

$Zn + 2OH^{-} = ZnO_2^{2-} + H_2$

These reactions are not affected by redox conditions.

4.1.4 Other metals

Lead will dissolve in some acids and is slowly attacked by cold alkali. Cotton *et al.* (1999) note that lead often appears to be more noble and unreactive than its standard half cell potential of -0.13V would suggest. This is attributed to a high overvoltage for hydrogen and, in some cases, to insoluble surface coatings. Lead does not dissolve in dilute sulphuric or concentrated hydrochloric acid (Cotton *et al.* 1999). Its resistance to corrosion has led to its widespread historic use in roofing, water pipework and the chemical industry.

Tin dissolves in some acids to form tin(II) and hydrogen, and is slowly attacked by cold alkali. It has a similar standard potential to lead.

Metallic copper is stable in water in the absence of oxygen and is unreactive towards non-oxidising acids in the absence of air. It readily dissolves in nitric acid and sulphuric acid in the presence of oxygen (Cotton *et al.* 1999). The standard half cell potential for copper is +0.34V and it is therefore more resistant to corrosion than lead. In the presence of sulphide, copper will react to form copper sulphide and hydrogen:

$2Cu + H_2S = Cu_2S + H_2$

However, sulphide will be scavenged from solution by the precipitation of sulphides of many other metals. Therefore, the amount of hydrogen evolved will depend on the water chemistry at the copper surface. The high resistance of copper to general corrosion in the absence of air at near-neutral pH values has led to its proposed use as a container material for the disposal of radioactive spent fuel and vitrified high-level waste (see, for example, Sjöblom *et al.* 1995).

Cadmium is similar in behaviour to zinc, reacting with non-oxidising acids to give hydrogen. However, it does not react with alkali. Mercury is inert to non-oxidising acids.

4.1.5 Galvanic processes

If an electrical circuit is created by the coupling of two dissimilar metals in the presence of water or other electrolytes, galvanic corrosion can occur. In this form of corrosion an electrical circuit is formed and a potential difference established. The less noble metal (the anode) is corroded more rapidly than it would in isolation, with a consequent increase in the rate of generation of hydrogen in the case of the metals considered here; the more noble metal (the cathode) corrodes less rapidly than it would in isolation.

Aluminium and zinc will corrode more rapidly if in contact with iron or steel. However, the electrochemical process will not change the amount of gas produced, merely the rate of generation.

4.2 Other chemical reactions producing gas

There are many possible chemical reactions other than corrosion that may take place in a mixed waste landfill to release gas. The disposal of traces of some reactive inorganic compounds will lead to their eventual hydrolysis and release of acid. Examples include the disposal of some halides and oxyhalides, e.g. SbF_5, and AsF_5. However, other halides such as SF_6 are unreactive.

4.2.1 Carbides

The reaction of some carbides with water or acid can generate simple hydrocarbons (Cotton *et al.* 1999).

Carbides containing C^{4-} ions (e.g. Be_2C and Al_4C_3) release methane on hydrolysis. For example:

$Al_4C_3 + 12H_2O = 4Al(OH)_3 + 3CH_4$

Carbides that can be treated as containing C_2^{2-} ions [e.g. $M(I)_2C_2$ where M(I) is an alkali metal or copper, silver or gold; $M(II)C_2$ where M(II) is an alkaline earth metal, zinc or cadmium); or $M(III)_2(C_2)_2$ where M(III) is aluminium, lanthanum or terbium] react with water to give acetylene (Cotton *et al.* 1999):

$CaC_2 + 2H_2O = HCCH + Ca(OH)_2$

The presence of carbides in salt slag wastes from aluminium recovery leads to the generation of hydrogen and methane when contacted with water (elemental hydrogen may also be produced from traces of elemental aluminium).

Some carbides do not fall into the two classes above. These include YC_2, TbC_2, YbC_2, LuC_2, UC_2, Ce_2C_2 and Tb_2C_2. These carbides are hydrolysed by water to give 50–70 per cent HCCH, though C_2H_4, CH_4 and H_2 are also produced.

Ternary carbides of the general formula A_3MC (A = rare earth or transition element, M = metallic or semi-metallic main group element) are hydrolysed by dilute hydrochloric acid to give mainly methane (~84–97 wt per cent) with the remaining products being saturated and unsaturated higher hydrocarbons (Cotton *et al.* 1999).

The carbides of the transition metals chromium (Cr_2C_3) and manganese, iron, cobalt or nickel (M_3C) are reported to be hydrolysed by water and dilute acids to give a mixture of hydrocarbons (including liquids and solids) and hydrogen (Cotton and Wilkinson 1972). However, there is some uncertainty about whether these transition metal carbides are reactive – essentially dependent upon whether interstitial on non-interstitial carbides are formed (Hoch *et al.* 2004). Thus, although these first row metal carbides may be unreactive in steels, it is possible they may be more reactive in slag and dross waste from the metal industries.

4.2.2 Reactions with acids

Carbon dioxide is a bulk constituent of landfill gas and is formed by microbial action, but it may also be formed by the reaction of carbonates with acid. In the laboratory, carbon monoxide may be prepared by the action of concentrated sulphuric acid on formic acid (Cotton and Wilkinson 1980). However, the thermal process described in Section 4.2.5 is likely to be the source of the low concentrations of carbon monoxide seen in gas from current landfills.

Hydrogen cyanide (HCN) is evolved when cyanides are treated with acid. Cyanides are present in a range of wastes including:

- those from the metallurgical industry such as electroplating wastes and aluminium potliner wastes (Grieshaber *et al.* 1994);
- in some contaminated soils.

Cyanogen [$(CN)_2$] could potentially be formed by the oxidation of cyanide. Contact of thiocyanates with acid can generate toxic gas.

Nitric oxide (NO) can be formed by reduction of nitric acid and solutions of nitrites and nitrates. It reacts with oxygen to form NO_2. Mixed oxides of nitrogen [NO_2 and N_2O_4 (NO_X)] are also formed from the reduction of nitric acid and nitrates. All these gases are toxic and reactive (Cotton *et al.* 1999).

Hydrogen sulphide is more toxic than hydrogen cyanide and is evolved from the reaction of metal sulphides with acids. Sulphides may be present in waste from industrial processes, or as a result of the production of hydrogen sulphide by microbial action which then reacts with metal ions.

Reactions between sulphuric acid and salts can result in the formation of hydrogen halides such as HF from reaction with calcium fluoride and HCl from reaction with sodium chloride.

4.2.3 Formation of phosphine, arsine and stibine

Phosphine (PH_3) can be generated by the reaction of some phosphides (e.g. those of alkali, alkaline earth and lanthanide metals) with water or acids. It is poisonous and readily oxidised by air when ignited, forming explosive mixtures with air when present at a sufficient concentration. Aluminium and magnesium phosphides are used as pesticides to fumigate grain; aluminium and zinc phosphides are used as rodenticides (DoH 2001).

Arsine (AsH_3) is a highly poisonous, colourless gas with an odour of garlic. It may be formed when inorganic arsenic is exposed to nascent (freshly formed) hydrogen or by the reaction of water with a metallic arsenide (DHHS 1979). Ores containing arsenic can liberate arsine if in contact with acid. Exposure to arsine has occurred during smelting and refining of metals. It has also been detected during galvanising, soldering, etching and lead-plating operations, and can also be produced by microbial action (see Section 4.3.2) in the presence of arsenic (DHHS 1979). Examples of industrial accidents cited in (DHHS 1979) involving the generation of arsine include:

- spraying of water onto slag to reduce dust hazard – the water reacted with alkali metal arsenide in the slag to generate arsine (Conrad *et al.* 1976);
- reaction of acidic arsenic liquor with the zinc coating of a galvanised bucket (Hocken and Bradshaw 1970);
- moisture reacting with aluminium arsenide in metal dross during the purification of lead alloys (Pinto *et al.* 1970);
- reclamation of metal from blast furnace flue dust by the addition of zinc, water and sulphuric acid (Jenkins *et al.* 1965);
- reaction of phosphoric acid with aluminium containing arsenic impurities (Elkins and Fahy 1967) and reaction of an aluminium ladder with sodium arsenic solution (Levinsky *et al.* 1970);
- washing of aluminium slag to dissolve soluble constituents – the copper in the mixture was contaminated with arsenic (Kipling and Fothergill 1964).

The basic chemistry in all these reactions is similar. Arsine is evolved when hydrogen is freshly formed in the presence of arsenic compounds or by the reaction of a metallic arsenide with water.

Antimony can be converted to stibine (SbH_3) by similar reactions. Stibine is at least as toxic as arsine, but is less stable (DHHS 1979).

4.2.4 Formation of metal carbonyls

Nickel tetracarbonyl [$Ni(CO)_4$] is used in the manufacture of catalysts and in nickel refining and purification. It is produced by passing carbon monoxide over finely divided nickel and is reportedly generated if carbon monoxide comes into contact with nickel in a reactive form (Hetland *et al.* 1991).

Traces of nickel tetracarbonyl [0.07–0.14 parts per billion (ppb) (v/v)] have been detected in sampled sewage gas (Feldmann 1999). The same study also found molybdenum hexacarbonyl [$Mo(CO)_6$, 0.25–0.30 ppb (v/v)] and tungsten hexacarbonyl [$W(CO)_6$, 0.0006–0.001 ppb (v/v)] in sewage gas. (These two latter compounds have also been detected in landfill gas at concentrations of 10–310 ng m^{-3} and 5–230 ng m^{-3} as molybdenum and tungsten respectively (Feldmann and Cullen 1997). No volatile species of iron, chromium, cobalt or manganese were detected.

Tests in a carbon monoxide atmosphere showed that $Ni(CO)_4$ was lost from the gas phase in the presence of deionised water, but not in the presence of nickel bromide solution, over a period of 11 weeks. The concentration of $Mo(CO)_6$ in carbon monoxide remained unchanged over the same period, whether in contact with deionised water or ammonium molybdate solution. $Fe(CO)_5$ was lost from the gas phase in the presence of both deionised water and a solution of iron sulphate (Feldmann 1999).

The mechanism of the formation of nickel carbonyl (chemical or microbially mediated) in sewage could not be identified (this was not the aim of the work); Feldmann notes that nickel carbonyl can be synthesised if nickel and sulphide are present in solution under a carbon monoxide atmosphere (Behrens and Eisenmann 1955).

Therefore, neither chemical nor microbial reactions can be eliminated as means of generating nickel carbonyl from sewage sludge or, by analogy, from landfills on the basis of current knowledge. Similarly, neither of these mechanisms for the production of molybdenum or tungsten hexacarbonyls can be eliminated. It is possible that $Fe(CO)_5$ may be formed in sewage gas but lost by reaction with aqueous solution.

4.2.5 Thermal processes

The carbon monoxide often found as a trace gas in current landfill gas is generally the result of thermal oxidation of organic material under sub-stoichiometric conditions (i.e. deficient in oxygen). Landfilled waste has a low thermal conductivity and hot spots may develop into sub-surface fires if the partial pressure of oxygen is relatively high. The source of the carbon may be organic solids, pyrolysis products or methane.

In partially saturated conditions, water gas – an equimolar mixture of carbon monoxide and hydrogen – may be produced by the reaction of steam with hot carbonaceous material. This process does not require oxygen, though air may be necessary for the process that generates the hot carbon.

Nitric oxide (NO) can be formed by thermal oxidation of nitrogen gas by the oxygen in air at high temperature (typically above 1000°C). It reacts with more oxygen to form NO_2.

4.2.6 Other reactions

Thermal and photochemical reactions of PVC result in the degradation of the polymer and the release of hydrogen chloride (Yassin and Sabaa 1990). Hence, stabilisers are included in the formulation of the PVC polymer for commercial use (White and Turnbull 1994). Vinyl chloride monomer (chloroethene) has been detected in landfill gas (Allen *et al.* 1997), although this is believed to arise through the biodegradation of chlorinated solvents rather than processes involving PVC.

Ammonia may be generated chemically by the reaction of an ammonium salt with base (Cotton and Wilkinson 1980):

$NH_4X + OH^- = NH_3 + H_2O + X^-$

or by the reaction of an ionic nitride with water, for example:

$Mg_3N_2 + 6H_2O = 3Mg(OH)_2 + 2NH_3$

Contact of water with salt slag wastes from aluminium recovery may generate ammonia.

Amines are released from the degradation of anion exchange resins (Baston *et al.* 1995, Biddle *et al.* 2002).

4.3 Microbial action and gas generation

4.3.1 Respiration

Some organic materials can undergo microbial degradation to produce gas under both aerobic and anaerobic conditions. The microbial degradation of MSW in landfills can be described by five idealised stages. There is an initial short period of aerobic degradation where oxygen trapped during waste deposition is utilised by aerobic microbes and CO_2 is produced. Anaerobic microbial activity then begins with the hydrolysis of organic materials and acetogenesis to release carboxylic acids (potentially decreasing the pH of the leachate) with production of hydrogen, ammonia and CO_2. Methanogenesis is then initiated and utilises carbon dioxide, hydrogen and acetic acid to produce methane. The rate of methanogenesis increases until a balance with the rates of hydrolysis and acetogenesis is achieved. The system is then at steady state and anaerobic degradation continues, producing a mixture of methane and carbon dioxide in the ratio of about 3:2. Finally, the organic substrate required for microbial activity becomes limited and the gas within the landfill returns gradually to atmospheric composition (Environment Agency 2004a).

Although the waste deposited in hazardous and non-hazardous landfills will contain little putrescible material, some cellulosic wastes such as paper, wood and cardboard will be present. Bottom ash from the incineration of MSW may contain traces of biodegradable organic material but the amounts are small (e.g. 1 per cent of the total organic carbon content of the residue) and it is rapidly degraded (Zhang *et al.* 2004). Though the microbial inoculum will also be much less than in MSW landfills, it cannot be assumed that microbial activity will not eventually take place in parts of a hazardous or non-hazardous landfill. However, the timescale over which this occurs and its extent may be uncertain.

Thus it is to be expected that mixed hazardous and mixed non-hazardous landfills will evolve carbon dioxide and methane to some extent. However, stable methanogenic conditions may not persist and it is probable that this gas will have a lower proportion of methane and higher than normal amounts of hydrogen as a result of the co-existence of both methanogenic and acetogenic conditions. Microbial processes may also generate smaller amounts of gases such as ammonia and hydrogen sulphide. Nitrogen oxides are also formed in small amounts from natural microbial processes.

Of the trace gases produced by microbial action, hydrogen sulphide is of particular interest because it is known to be a component of gas from existing landfills and is toxic. Although the presence of sulphides in waste disposed to future landfills indicates that chemical generation of hydrogen sulphide is also possible (see Section 4.2.2), reduction of sulphate by sulphate-reducing bacteria (SRB) is likely to be the major source. Hydrogen sulphide dissolves in water to give a ~0.1 mol dm^{-3} solution under 1 atmosphere pressure (Cotton *et al.* 1999) and behaves as a weak acid. H_2S is the dominant dissolved species below ~pH 7 whereas HS^- becomes the major species under most alkaline conditions of interest. The sulphides of many trace metals of environmental interest (e.g. mercury) have very low solubility.

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 landfill gas. The reaction between hydrogen sulphide and ferrous iron in aqueous solution at neutral pH yields amorphous iron sulphide (approximately FeS), although its exact composition has been the subject of extensive discussion. Crystalline iron sulphides generally found in nature are mackinawite ($Fe_{0.995\text{-}1.023}S$), greigite (Fe_3S_4) and pyrite (FeS_2). Amorphous FeS may be a mixture of fine-grained mackinawite and greigite. It has been suggested that the formation of mackinawite (and probably amorphous iron sulphide) proceeds via the reactions:

$Fe^{2+} + SH^- = FeSH^+$

$2\ FeSH^+ = Fe_2S_2 + 2\ H^+$

nFe_2S_2 = mackinawite

The reaction of hydrogen sulphide with goethite over the pH range 7 to 8.5 may give iron(II) and elemental sulphur and polysulphides as the reaction products (Morse *et al.* 1987). It has been shown that the dissolution rate of iron (II) and iron (III) (hydr)oxides is increased by about two orders of magnitude in the presence of hydrogen sulphide at pH 7 (Keresztes *et al.* 2001).

Hydrogen sulphide is known to act as a corrosive contaminant of fluids in a variety of industrial situations. In many cases, this arises from microbial action by SRB, although the unpredictability of the occurrence and effect of hydrogen sulphide from microbial process can add to the complexity of interpreting observations in experiment or real-life situations (Edyvean 1991). Hydrogen sulphide concentrations of between 50 and 200 ppm may be typical of the concentration at a metal surface in the presence of active SRB.

Damage to steels due to SRB results mainly from the generation of hydrogen sulphide and consequent corrosion by sulphide ions. Another influence is the formation of iron sulphide (FeS) films on the metal as thin adherent films tend to protect the metal from corrosion. However, corrosion occurs when such films are disrupted (e.g. by microbial action or the presence of oxygen) or when ferrous iron is present in solution at high enough concentrations to result in the formation of a loose sulphide film. Other solutes also affect the nature of the sulphide film as the presence of a range of surface deposits in mixed systems can increase the rate of corrosion at a particular hydrogen sulphide concentration, presumably through disruption to (or discontinuity in) the iron sulphide film (Edyvean 1991).

Mild steel undergoes pitting corrosion under alkaline conditions if the concentration of HS^- is much greater than the concentration of OH^- (Salvarezza *et al.* 1982). Corrosion of carbon steel in oxygen-free deionised water under acidic conditions imposed by high pressures of H_2S (1.5 MPa) resulted in the formation of a range of iron sulphides, from mackinawite to pyrite, depending on temperature (308–433K) and exposure time (1–840 hours) (Wikjord *et al.* 1980). The overall corrosion reaction is:

$Fe + 2 H_2S = Fe^{2+} + 2SH^- + H_2$

with the ferrous ions either forming iron sulphide phases or passing into bulk solution. Inhibition of iron corrosion by hydrogen sulphide in acid solution has been found to occur over a narrow pH range (3–5) at concentrations below 4×10^{-5} mol dm^{-3} hydrogen sulphide (Ma *et al.* 2000).

Thus, as well as reacting with dissolved metal ions to form insoluble sulphides, hydrogen sulphide can be directly involved in the corrosion of metallic iron and steel. It is likely that iron sulphide films formed under the solution conditions in a landfill cell will not be protective because of the variety of possible surface deposits. Therefore, metallic iron and steel can act as chemical ‘sinks’ for hydrogen sulphide under both acidic and alkaline conditions. However, their effectiveness will depend on:

- the partitioning of hydrogen sulphide between the gas and aqueous phases;
- the rate of reaction compared with the rate of the hydrogen sulphide generation;
- the distribution of iron and steel relative to sources of hydrogen sulphide.

4.3.2 Biosubstitution

The possibility of the formation of metal carbonyls through microbially-mediated reactions is mentioned in Section 4.2.4. Biomethylation of a range of metals and metalloids is also possible.

Feldmann (2003) reports that $(CH_3)_2Se$, $(CH_3)_3As$, $(CH_3)_2AsH$, CH_3AsH_2, AsH_3, $(CH_3)_4Sn$, $(CH_3)_2(C_2H_5)_2Sn$, $(CH_3)_3Sb$, $(CH_3)_2Te$, CH_3I, $(CH_3)_2Hg$, $(CH_3)_4Pb$, $(C_2H_5)_3CH_3Pb$ and $(CH_3)_3Bi$ (as well as the carbonyls mention above) can be found in environments such as municipal waste deposits or anaerobic digestion of sewage sludge.

Hirner (2003) identifies the most important criteria for a high biomethylation potential as:

- an anaerobic atmosphere (at least on a microscale), reducing conditions and slightly acidic pH values in the hydrosphere;
- metal(loid)s in easily accessible forms (e.g. as ions);
- the presence of microorganisms with biomethylation potential (bacteria; fungi, algae, archeae);
- the presence of transferable methyl groups.

Microbial methylation or alkylation of arsenic has been reviewed extensively (Bentley and Chasteen 2002). The major volatile products formed by biomethylation are:

- CH_3AsH_2 (monomethylarsine)
- $(CH_3)_2AsH$ (dimethylarsine)
- $(CH_3)_3As$ (trimethylarsine).

Non-volatile compounds (methylarsonate and dimethylarsonate) are also formed.

Bioalklyation is used to refer to the processes involving alkyl groups other than methyl and there is evidence of this process for arsenic. Bentley and Chasteen (2002) note that $As(C_2H_5)(CH_3)_2$ has been found in landfill and sewage gas, while $As(C_2H_5)_3$ has been found in landfill gas (Feldman and Hirner 1995). Arsine, monomethylarsine, dimethylarsine and trimethylarsine have been detected in the headspace above incubated sewage sludge samples (Michalke *et al.* 2000) (Table 4.3) and in gas from anaerobic municipal waste landfills (concentration range of $\mu g\ m^{-3}$) (Feldmann and Cullen 1997).

Table 4.3 Metal(loid) content of sewage sludge and volatile metal(loid)s detected in the headspace of incubated sewage sludge after 1 week at 37ºC[1,2]

Element	Concentration in sludge (10^{-3} g kg^{-1} dry weight)	Volatile species	Concentration of element in headspace (10^{-6} g m^{-3})
Te	0.2 ± 0.1	$(CH_3)_2Te$	1.9 ± 0.15
Bi	1.4 ± 0.3	$(CH_3)_3Bi$	46.2 ± 6.9
Se	1.5 ± 0.5	–[3]	
Sb	1.7 ± 0.3	$(CH_3)_3Sb$[4]	77.5 ± 4.6
Hg	3.0 ± 1.2	Hg^0	0.29 ± 0.16
As	15.2 ± 1.3	AsH_3	0.76 ± 0.21
		CH_3AsH_2	0.68 ± 0.45
		$(CH_3)_2AsH$	0.51 ± 0.36
		$(CH_3)_3As$	3.3 ± 1.3
Sn	25.4 ± 0.3	$(CH_3)_4Sn$	0.29 ± 0.18

Notes:

[1] Michalke *et al.* (2000)

[2] The experiments contained 50 cm^3 of sludge (2 per cent wt/vol dry matter) in 120 cm^3 bottles under a CO_2/H_2 (20:80 v/v) atmosphere at 200 kPa.

[3] No volatile Se species detected, although dimethyl selenide and dimethyl diselenide were detected above pure cultures incubated with 0.1 mol dm^{-3} Se.

[4] Stibine, monomethylstibine, dimethylstibine and trimethylstibine detected above pure culture of *Methanobacterium formicicum* incubated with 0.005 mol dm^{-3} Sb.

Bentley and Chasteen (2002) cite studies showing evidence for biomethylation of antimony. For example, trimethylstibine [$(CH_3)_3Sb$] was produced by the action of fungi on trimethylstibine dihydroxide [$(CH_3)_3Sb(OH)_2$], demonstrating reduction of antimony(V) to antimony(III) (Barnard 1947), and trimethylstibine was detected above enriched soil cultures under anaerobic conditions (Gürleyük *et al.* 1997, Jenkins *et al.* 1998). Trimethylstibine has also been detected in the headspace above incubated sewage sludge samples (Michalke *et al.* 2000). Stibine, monomethylstibine, dimethylstibine (and trimethylstibine) were also detected in some of these experiments after short incubation periods of 15 hours, but appeared to be short-lived; only trimethylstibine was detected after incubation for 5 days (Michalke *et al.* 2000). Trimethylstibine has also been detected in gas from anaerobic municipal waste landfills (concentration range of $\mu g\ m^{-3}$) (Feldmann and Cullen 1997).

Trimethylbismuth has been detected in gas from anaerobic municipal waste landfills (concentration range of ng m^{-3}) (Feldmann and Cullen 1997). Bentley and Chasteen (2002) record that trimethylbismuth has been identified in landfill and sewage gas (Feldman and Hirner 1995, Michalke *et al.* 2000).

Bentley and Chasteen (2002) noted that triethyllead is a metabolic product of tetraethyllead (Griffiths and Usta 1988) and volatile lead species with methyl and ethyl groups have been detected in sewage gas (Feldman and Hirner 1995). Tetramethyllead and tetraethyllead have been detected in gas from anaerobic municipal waste landfills (concentration range of ng m^{-3}) (Feldmann and Cullen 1997).

Dimethyltellurium has been detected in the headspace above incubated sewage sludge samples (Michalke *et al.* 2000). Dimethylselenuium and dimethyldiselenium were also detected in the same work above pure cultures, though they were absent in sewage gas (Michalke *et al.* 2000). Dimethylselenide and dimethyltellurium have been detected in gas from anaerobic municipal waste landfills (concentration range of ng m^{-3}) (Feldmann and Cullen 1997).

Tetramethyltin has been detected in the headspace above incubated sewage sludge samples (Michalke *et al.* 2000). Five volatile tin species (tetramethyltin and four higher alkylated tin species) have been detected in gas from anaerobic municipal waste landfills (concentration range of µg m^{-3}) (Feldmann and Cullen 1997).

Work with pure cultures has shown microbially mediated reduction of mercury(II) to elemental mercury (Michalke *et al.* 2000). Dimethylmercury and elemental mercury have been detected in gas from anaerobic municipal waste landfills (concentration range of ng m^{-3}) (Feldmann and Cullen 1997). Another study found that total gaseous mercury at several municipal landfill sites in Florida, USA, is present at concentrations in the range 10 to 12,000 ng m^{-3} while methylated mercury compounds occur at typical concentrations of up to tens of ng m^{-3} (Lindberg *et al.* 2005). Dimethylmercury was the predominant methylated species, at concentrations of 4.5–77 ng m^{-3}, with the concentrations of monomethyl mercury lower at 1.7 –39 ng m^{-3}. There was no simple direct relationship between the concentrations of mono- and dimethyl mercury. In addition, the proportion of methylated mercury ranged from <0.05 per cent to 50 per cent of the total gaseous mercury.

In the same study, gas was sampled from the Hamilton Landfill in California. Although total gaseous mercury was present in the sampled gas at a concentration of 4700 ± 3700 ng m^{-3} (within the range determined for the Florida landfills), the concentration of dimethyl mercury was below the detection limit at <0.03 ng m^{-3}. There may be a number of reasons for the lack of methylated mercury at the Hamilton Landfill. It had received mainly commercial and demolition waste rather then municipal waste, and been closed since 1974. Therefore, it was expected to be past the peak rate in methane production. In addition, the waste was mostly saturated with groundwater and was deposited in a layer only 5–8 feet (≈1.5–2.5 m) thick.

Measurements at three UK landfills that had accepted wastes with relatively high mercury levels found typical total gaseous mercury concentrations in the range 6 to 130 ng m^{-3} with organic mercury concentrations in these samples below the detection limit of 35 ng m^{-3} (ESART 2003). A comparison of these data with other studies found the total gaseous mercury concentration to be within the ranges reported elsewhere, apart from studies by Lindberg *et al.* (2001) from sites in Florida which are an order of magnitude higher. Concentrations of organic mercury below the detection limit of the ESART study are not inconsistent with the observations made by Lindberg *et al.* (2005).

Table 4.4 shows the concentrations of arsine, elemental mercury and various methylated and alkylated species in landfill gas sampled from gas wells or above wetland (through which the gas had percolated) at a municipal waste landfill in Canada. Concentrations ranged from 1×10^1 to 2×10^5 ng m^{-3} with the most abundant species being trimethylstibine and tetramethyltin.

The stabilities of SbH_3, CH_3SbH_2, $(CH_3)_2SbH$, $(CH_3)_3Sb$, AsH_3, CH_3AsH_2, $(CH_3)_2AsH$, $(CH_3)_3As$, SnH_4, $(CH_3)_4Sn$, $(CH_3)_2SnH_2$, $(CH_3)_3SnH$ and $(C_4H_9)SnH_3$ at concentrations of 10 µg m^{-3} have been measured in air at 20°C and 50°C in the dark, and at 30°C exposed to ultraviolet (UV) light (Feldmann 2003). The estimated half-lives decreased with the increase in temperature or exposure to UV light. For example, the half-life of stibine was approximately 2,000 hours at 20°C in the dark, 600 hours at 50°C in the dark and 1 hour at 30°C exposed to UV light at 5,000 lux. A full list of the estimated half lives is given in Table 4.5.

Methylated sulphur species detected in landfill gas are methyl mercaptan, dimethylsulphide and dimethyl disulphide (carbon disulphide and hydrogen sulphide were also found) (Kim *et al.* 2005).

It is possible that a number of other elements may be methylated under appropriate conditions. These include zinc, cadmium, thallium, silicon and germanium. No data have been found for the presence of these elements in landfill gas but Hirner (2003) notes that many organometalloid species remain to be identified in samples taken from various environments.

Table 4.4 Volatile metal(loid) compounds detected in landfill gas and above wetlands at a municipal waste landfill in Canada[1]

Species	Concentration (10^{-9}g m^{-3})[2]	
	Landfill gas	Above wetland
AsH_3	7×10^1	1×10^2
CH_3AsH_2	4×10^2	8×10^2
$(CH_3)_2AsH$	1×10^1	2×10^2
$(CH_3)_3As$	4×10^3	5×10^2
$(CH_3)_2As(C_2H_5)$	4×10^1	-
$(CH_3)_3Sb$	1×10^5	2×10^5
$(CH_3)_4Sn$	1×10^5	3×10^4
Sn(U1) 3)	8×10^3	5×10^3
Sn(U2) 3)	8×10^3	4×10^3
Sn(U3) 3)	9×10^3	4×10^3
Sn(U4) 3)	8×10^3	1×10^3
$(CH_3)_3Bi$	1×10^3	6×10^2
Hg(0)	9×10^2	2×10^3
$Hg(CH_3)_2$	1×10^2	5×10^1
$(CH_3)_2Te$	1×10^2	1×10^2
$(CH_3)_2Se$	2×10^1	3×10^1
$Pb(CH_3)(C_2H_5)_3$	4×10^1	2×10^1
$Pb(C_2H_5)_4$	1×10^3	7×10^2

Notes:

[1] Feldmann (2003)

[2] All concentrations estimated from Figure 2 in Feldmann (2003) and quoted to one significant figure.

[3] Sn(U1–U4) = unknown R_4Sn species

Table 4.5 Estimated atmospheric half-lives of volatile metal(loid) compounds in air in the dark and exposed to ultraviolet light[1]

Species	Half life (hours)[2,3]		
	Dark, 20°C	Dark, 50°C	UV[4], 30°C
SbH_3	2×10^3	7×10^2	1×10^0
$(CH_3)SbH_2$	1×10^3	3×10^2	1×10^{-1}
$(CH_3)_2SbH$	1×10^2	6×10^1	1×10^{-1}
$(CH_3)_3Sb$	5×10^1	6×10^0	1×10^{-1}
AsH_3	2×10^3	6×10^2	2×10^2
$(CH_3)AsH_2$	1×10^3	6×10^2	2×10^0
$(CH_3)_2AsH$	5×10^2	9×10^1	1×10^{-1}
$(CH_3)_3As$	-	3×10^1	1×10^{-1}
SnH_4	2×10^3	8×10^2	1×10^0
$(CH_3)_2Sn_2H_2$	1×10^3	5×10^2	1×10^1
$(CH_3)_3SnH$	8×10^2	2×10^2	6×10^0
$(C_4H_9)SnH_3$	1×10^3	6×10^2	5×10^0

Notes:

[1] Feldmann (2003)

[2] All half lives estimated from Figure 3 in Feldmann (2003) and quoted to one significant figure.

[3] In synthetic air atmosphere

[4] UV radiation at 5,000 lux (5,000 lm m^{-2}). Direct sunlight in summer has an illuminance of up to 100,000 lux whereas on a cloudy day a value of 1,000 lux may be typical. One lumen at a wavelength of 5,500Å (green light) ≈ 0.0015 W. A typical wavelength for UV light from a mercury lamp is ≈ 2,500 Å. Thus 1 lumen of UV light has approximately twice the power of 1 lumen of green light. Note that photolytic degradation requires the absorption of energy and thus the wavelength of light may be important.

4.3.3 Bioreduction of phosphorus to phosphine

Phosphine (PH_3) is present in biogas from a variety of sources including landfills. Phosphine concentrations of 3–32 µg m^{-3} (as phosphorus) have been measured in landfill gas at the Hooge Maey Landfill in Flanders, Belgium (Roels and Verstraete 2004) (Table 4.6).

There has been some debate about possible mechanisms for the production of phosphine; microbial reduction of phosphate to phosphine or release of reduced phosphorus as phosphine have been suggested. The reduction of phosphate to phosphine is thermodynamically unfavourable (Roels and Verstraete 2001). Their experiments showed that phosphine can be generated by chemical release from iron and aluminium metals and that microbial process, particularly those enhancing corrosion, could be instrumental in enhancing such releases of phosphine (Roels and Verstraete 2004). They estimated that the corrosion of 1 kg of metal (aluminium or iron) results in the formation of 1 mg of PH_3 and that 160 g of phosphine is released in 1.75×10^7 m^3 of biogas per year from the Hooge Maey Landfill, corresponding to the corrosion of 160 tonnes of metal (0.15 per cent of the estimated total metal in the landfill).

Subsequent work by the same research team has strengthened the view that respiratory reduction of phosphate to phosphine is unlikely. Phosphine is generated by chemical acid corrosion and microbial corrosion. Microbial action is apparently capable of reducing phosphorus(zero valent) in the steel to phosphine, as the amount of phosphine generated in microbial experiments exceeds the amount of iron phosphide in the steel (Roels *et al.* 2005).

Table 4.6 Phosphine concentration in landfill gas extracted from the Hooge Maey Landfill, Flanders, Belgium[1]

Well number	Phosphine concentration as P (10^{-6} g m^{-3})
1	4.1 ± 0.6
2	7.7 ± 1.8
3	7.0 ± 1.2
4	6.7 ± 0.7
5	7.9
6	8.0 ± 0.4
7	7.4 ± 1.3
8	6.4 ± 0.1
9	9.7 ± 0.5
10	6.1 ± 2.3
11	32.4 ± 1.0
12	9.1 ± 0.8
13	32.3
14	13.7 ± 1.2
15	6.8 ± 0.2
16	14.7 ± 0.9
17	8.1 ± 0.5
18	7.5 ± 0.8
19	3.2
20	9.1 ± 0.4
21	8.4 ± 0.5
22	6.0 ± 1.0
23	8.7 ± 0.5
24	18.5

Notes: [1] Roels and Verstraete (2004)

4.4 Volatilisation of 'as-disposed' materials (mercury, some inorganic compounds and organic compounds) and miscellaneous reactions

There are a large number of species that could be volatilised from waste due to the disposal of traces of materials with high vapour pressures; the majority of these are organic compounds.

Methylation of mercury is discussed in Section 4.3.2; inorganic mercury was the dominant component of the total gaseous mercury from many of the landfills sampled in by Lindberg *et al.* (2005).

Carbon disulphide (CS_2) has been reported in the landfill gas from MSW. It is highly flammable and very reactive. When impure it has a strong odour. At room temperature, it is very volatile and is classified as a VOC. In industry it is used in the production of cellulose rayon fibres, cellophane and carbon tetrachloride, and is also used as a solvent. Small amounts are generated naturally over marshes. Its source in gas from MSW landfills is unclear, but it may be an end product of microbial action on sulphur compounds in the waste. It breaks down rapidly in the environment (Environment Agency 2005b); CSe_2 also exists with a stronger odour than CS_2 but is not flammable and slowly polymerises (Cotton *et al.* 1999).

Siloxanes may be present in landfills through the disposal of consumer products, commercial lubricants and wastewater treatment sludges. Some of these species may be volatile and it is also possible that non-volatile, high molecular weight organic silicon compounds may be degraded to form lower molecular weight volatile species. Concentrations of >1 to <100 parts per million (ppm) organic silicon have been found in landfill gas. Siloxanes are of interest as a trace component of gas from existing landfills because they are converted to inorganic siliceous deposits in landfill gas engines and reduce engine life (Environment Agency 2004c).

A large number of other trace organic compounds have been detected in gas from municipal waste landfill sites (Allen *et al.* 1997, Environment Agency 2002a, Environment Agency 2003b). Many of these are xenobiotic organic compounds which are also found in landfill leachates with possible origins in hazardous household waste (Slack *et al.* 2005); the compounds found in leachates are listed in Appendix B. Many of them would also be expected in gas released from hazardous and non-hazardous waste landfills containing wastes from, for example, the organic chemical, pharmaceutical, plastic and paint industries.

The organic chemicals may also react in a landfill to form other substances that may be more hazardous, for example:

- the formation of phosgene from oxidation or thermal decomposition of chloroform;
- the reaction of chloroform with acetone in the presence of alkali
- the reaction of chlorinated solvents with some metals.

The likely dominant volatile organic species from wastes disposed to primarily inorganic landfills in the future could be estimated from knowledge of the organic-containing (e.g. solvent-containing) wastes consigned for disposal.

5 Potential volatile products

5.1 Bulk gases

A broad classification of the types of waste going to inorganic landfill and their potential contaminants are listed in Table 5.1. Tables 3.4 and 3.5 give typical elemental concentrations in APC residues and in a sample of MSW incinerator bottom ash respectively. Table 3.6 gives concentrations of species in leachate from an inorganic waste test cell. This information together with the discussion in Section 4 allows a number of likely products from reactions in hazardous and non-hazardous landfills to be identified (see Table 5.2).

Table 5.1 Types of waste going to inorganic landfill and potential contaminants[1]

Treated waste going to inorganic landfill	May contain:
Contaminated soil	As, Sb, hydrocarbons, cyanides, organochlorines, ammonium, Fe, Zn, heavy metals
Asbestos	
Fragmentiser wastes	Oils, glass fibre, metal fragments, plastics
Incinerator residues	Metals, oxides, hydroxides, residual and part-combusted organics
APC residues	Lime, calcium sulphate, chloride and sulphate, contamination with mercury, etc.
Scrap from waste electrical items	Copper, lead, selenium, plastics, general metal
Bulky industrial items (filter housings, ducts, process equipment)	Metals plastic composites with organic contamination
Contaminated demolition rubble	As, Sb, hydrocarbons, organochlorines, Fe, Zn, heavy metals
Used lime	Lime, calcium sulphate, chloride and sulphate, contamination with organics and other metals
End-of-life vehicle (ELV) residues	Mixed plastics, metal, oils
Neutralisation sludges	Sulphates, hydroxides, residual organics and heavy metals
Used filter media	IX resins, activated carbon, inorganic sorbents with heavy metals and organics
Cemented wastes	As APC residues
Reject products	Composite materials with plastics and metals
Furniture and fittings	Medium density fibreboard (MDF), organics, metal fittings
Batteries	Cd, Pb, Ni, Zn
Swarfs from metal finishing	Ferrous metals and oil
Tins containing solvent based paints and varnishes	Tin compounds coated iron plus solders plus hydrocarbons
Dredgings	Metal sulphides, tin, organics
Tins contaminated with oils, biocides, pesticides, etc.	Tin compounds coated iron plus solders plus trace organics

Notes: [1] Professional judgement by A. Rosevear provided as a personal communication.

The bulk gases produced from inorganic landfills (hydrogen, carbon dioxide, methane) are potentially the same as those from existing MSW landfills (see Section 4). However, the quantities of gas produced and their rates of production are likely to be different from MSW landfills due to the different waste inventories and consequently different chemical conditions and microbial environments.

The amount of hydrogen produced will be determined by the corrosion of three metals (iron present in steels, aluminium and zinc). 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 the leachate (e.g. chloride) or physical contact with other metals (galvanic corrosion). In addition, the evolution of hydrogen from iron requires anaerobic conditions. Illustrative calculations to determine the onset of anaerobic conditions and the rates of generation of hydrogen from iron, zinc and aluminium corrosion are described in Section 6. The overall amounts of hydrogen produced from the corrosion of aluminium and zinc are determined by the total amounts of these metals available in a landfill. The amount of hydrogen produced from the corrosion of iron and steel depends on their inventory and the onset of anaerobic conditions at the metal surface.

Although carbon dioxide can be evolved from the reaction of carbonates with acids, the amounts produced will depend on the proximity of acids to carbonate-containing wastes. If wastes are suitably conditioned such that acids are not disposed of directly (as required by the Landfill Directive), then sources of acids would be from degradation of some wastes. Therefore, production of carbon dioxide through reaction of acids with carbonates is likely to be relatively slow (where it occurs) and will not occur in regions of a landfill or for particular types of landfill where carbonates are not present. In addition, the presence of alkaline solids may prevent acidic solutions reaching carbonate wastes or may minimise release of carbon dioxide by their carbonation or dissolution of carbon dioxide in alkaline solutions with possible precipitation of calcium carbonate.

The typical mixed non-hazardous waste inventory estimated in Section 3.2.2 shows that cellulosic wastes (wood, paper, cardboard) are present at about 14 per cent of the waste by mass. Thus, for this type of landfill, the production of carbon dioxide from microbial degradation is likely but, because putrescible materials are excluded, the rates of generation will be lower than from a MSW landfill. In the mixed hazardous waste inventory, the estimated amount of wood and paper is much lower (0.2 per cent). Some contribution to the amount of carbon dioxide would also be expected from microbial action on some of the other waste organic materials (e.g. small organic compounds, fats, etc.). However, these are only estimated to be present in relatively small amounts in the mixed hazardous and non–hazardous waste inventories. The inert waste, asbestos waste and gypsum waste may also contain a small amounts of wood, paper and cardboard and therefore generate carbon dioxide slowly from low rates of microbial action. These latter wastes are all expected to be alkaline and therefore the release of free carbon dioxide should be minimised by carbonation reactions within the landfill cells.

Similar arguments to those above for carbon dioxide can also be made when considering methane generation. Although the reactions of some carbides with water can release methane (and other simple hydrocarbons), this should be a relatively small source of methane in mixed waste as reactive carbides should not be present in more than trace amounts (e.g. in metallurgical refining wastes). Thus the main source of methane is expected to be from the degradation of organic materials in the waste once methanogenesis has occurred and anaerobic microbial degradation established. Microbial reduction of carbon dioxide by hydrogen arising from corrosion could lower the relative concentration of carbon dioxide. In the absence of metal corrosion, the onset of anaerobic activity would depend on the rate of oxygen ingress though the landfill cap compared with the rate of microbial action. Thus, for an inert landfill where there is no capping requirement (see Table 2.1) it is unlikely that anaerobic conditions would be established. As microbial action will be much slower than in a MSW landfill, it is possible that anaerobic activity might not be established in other types of inorganic landfills – or regions of individual landfills – in the absence of metal corrosion. It is also possible that, once metal corrosion has ceased, the rate of microbial activity would be insufficient to maintain anaerobic conditions. Finally, the presence of chemicals such as nitrate, sulphate and sodium hypochlorite can inhibit or prevent methanogenesis (Environment Agency 2004a) either by acting as electron acceptors or through their biocidal action.

Thus it can be expected that:

- the rate of bulk gas generation will be much lower than from MSW landfills;
- the ratio of hydrogen: methane: carbon dioxide will be different with the probability of the gas having a higher ratio of hydrogen – and possibly a lower ratio of methane – compared with carbon dioxide.

The lower rates of gas productions will mean that residence times of reactive gases in inorganic landfills should be longer than in MSW landfills. Therefore, there will be more opportunity for gases such as hydrogen chloride and other hydrogen halides, hydrogen sulphide and carbon disulphide to dissolve in the landfill leachate or react with waste solids in the landfill (e.g. reaction of acids with metals, cement and concrete or the precipitation of metal sulphides).

If equilibrium can be assumed, it is possible to calculate the ability of the contents of a landfill to remove acids based on the amounts of metal or cement in the wastes compared with the total acid generation potential of the waste (some simplifying assumptions may need to be made to deduce the acid yield). Such an approach would be similar, for example, to calculating the amount of cement required to maintain high pH in a radioactive waste repository (Harris 1997, Gould *et al.* 2001). However, the distribution of wastes may be highly heterogeneous in many landfills and it may be necessary to consider reactions over a smaller scale (Chambers *et al.* 2004).

As well as chemical reactions between gases, solids and dissolved species in a landfill, other gases may be adsorbed onto solids in the landfill, for example volatile organic species may be sorbed to clays and soils (Biddle 1989). Although such reactions may be reversible, they would hinder the rate of release of volatile species and may also provide an opportunity for degradation (e.g. by microbial action in soils). The use of clays in landfill liners and caps will retard the release of some volatile species, as will the soil in which the landfill cell is located and any soil used above the landfill to restore the site. In addition, the sorption and relatively low flux will allow a greater degree of biological oxidation of VOCs within biofilms that may be present on the cover materials. Other components of the landfill engineering (e.g. synthetic polymer liners) may be degraded by some inorganic and organic gases and vapours, but this could not be considered to offer a useful sink for such gases.

Table 5.2 Potential gases from disposal of inorganic wastes

Element	Gas	Melting point (°C)	Boiling point (°C)	Comments
Antimony	SbH_3 stibine	–89	–17	Colourless gas, poisonous. Less stable than arsine, strong reducing agent. Used as dopant in semiconductor industry. May be formed during battery overcharging or when antimony compounds come into contact with acid plus a reducing agent. Possible microbial generation.
	Alkylated Sb compounds	–	–	Formed by microbial action.
Arsenic	AsH_3, arsine	–114, –117	–55, –62	Colourless gas, poisonous, pyrophoric. Thermally unstable, decomposes on hot surfaces to arsenic (Marsh test). Strong reducing agent. Used in organic synthesis and semiconductor industry. May be formed from arsenic-containing wastes by chemical or microbial routes.
	Alkylated As compounds			Formed by microbial action.
Bismuth	BiH_3			Very unstable, unlikely to be important
	Alkylated Bi compounds			Microbial action
Bromine	Br_2	–7	59	Reactive. Possible presence in waste
	HBr			From reaction of salts with acid
Carbon	CO	–199	–192	Poisonous gas, trace in MSW landfill gas from hotspots.
	CO_2	–57	–79 subl	Colourless gas, soluble in water. Generated by aerobic and anaerobic action in MSW. Also from reaction of acids with carbonates.
	$COCl_2$ phosgene	–104	8	Poisonous colourless gas. Decomposes in contact with water. Used in manufacture of intermediates for polyurethane, polycarbonate and dyes. May be formed by reactions of chlorinated solvents.
	Simple hydrocarbons			Microbial action on organic wastes, carbides.
Chlorine	Cl_2	–101	–35	Reactive
	HCl			From reaction of salts with acid
Fluorine	F_2	–220	–188	Poisonous. Reactive
	HF			From reaction of salts with acid
Germanium	Germane, GeH_4	–165	–89	Colourless gas, pyrophoric. Used in semiconductor industry. No evidence found on production in natural systems.
	Alkylated Ge compounds			$Ge(CH_3)_4$ used in semiconductor industry.
Hydrogen	H_2	–259	–253	Colourless gas. Flammable, produced by metal corrosion and microbial action.

Table 5.2 (cont'd) Potential gases from disposal of inorganic wastes

Element	Gas	Melting point (°C)	Boiling point (°C)	Comments
	HCN	–14	26	Colourless gas, highly soluble, poisonous. Used in manufacture of acrylonitrile, plastics, KCN, NaCN and in electroplating. Liberated by action of acid on cyanide containing wastes.
Iodine	I_2	114	184	
	HI			
Lead	Plumbane, PbH_4			Unstable, unlikely to be important
	Alkylated Pb compounds			Disposal and possible microbial action
Mercury	Hg	–39	357	Disposal and reduction of mercury compounds
	Alkyl Hg compounds			From microbial action
Nickel	$Ni(CO)_4$	–25	43	Colourless/yellow volatile inflammable liquid or needles, oxidises in air to NiO and CO_2. Pyrophoric flashpoint –20°C. Traces formed by reaction in landfill between CO and Ni, possibly via microbial action.
Nitrogen	NH_3, Ammonia	–78	–33	Colourless gas, microbial action
	$(CN)_2$, cyanogen	–28	–21	Colourless gas pungent odour, very poisonous, slowly hydrolysed by water. Used in chemical synthesis and a possible soil fumigant.
	NO	–164	–152	Unstable, decomposes to N_2O and NO_2 at high pressures at 30–50°C. Reacts with O_2.
	N_2O	–91	–89	Relatively unreactive,. Used as anaesthetic and propellant gas,. Formed by microbial action
	NO_2	–11	21	Reacts with water to give nitric and nitrous acids.
	Amines			
Phosphorus	PH_3, phosphine	–134	–87	Colourless, poisonous, inflammable gas due to traces of P_2H_4 or P_4, strong reducing agent, slightly soluble. Produced by reaction of phosphides with water or acid and by microbial action coupled with metal corrosion.
Selenium	H_2Se	60.4?	–42	Colourless gas, poisonous. Soluble in water. Reaction of some selenides with acid and by microbial action (cf. H_2S)
	CSe_2	–46	125	Non-flammable, strong odour. Possibly formed by same route as CS_2.
	COSe	–124	–22	Decomposes in contact with water, colourless gas, very poisonous. Possible trace formed by microbial action cf. COS?

Table 5.2 (cont'd) Potential gases from disposal of inorganic wastes

Element	Gas	Melting point (°C)	Boiling point (°C)	Comments
	Alkylated selenium cpds			Microbial action
Silicon	Silane			Flammable explosive mixtures with air, decomposes slowly on contact with water, odour
	Alkylated silicon compounds			Toxic, flammable, explosive mixtures with air, decompose on contact with water
	Siloxanes		–	Used in consumer products.
Sulphur	H_2S	–86	–61	Colourless gas, inflammable, soluble in water, poisonous. Formed by microbial action on sulphate under anaerobic conditions and acids on sulphides. Prevented from microbial formation by presence of nitrate, etc.
	SO_2	–10	–76	Gas, quite soluble in water.
	HSCN (HNCS), thiocyanic acid (iso)	>–110	Polym to solid –90	Colourless mass or gas, very soluble in water. Thiocyanates used in the manufacture of chemicals, pesticides, dyes, electroplating and photographic industries. Formed by reaction of salts with acids.
	Alkylated sulphur compounds			Industrial use and also formed by microbial action.
	CS_2	–111	46	Highly flammable, very reactive, strong odour. Flashpoint = –30°C, slightly water soluble. Used as disinfectant, bactericide, preservative, solvent chemical reagent. Formed by microbial action.
	COS	–138	–50	Flammable and toxic, unpleasant odour, corrosive to common metals when moisture present. Used in synthesis of thioacids, etc. Plays role in microbial sulphur cycling.
Tellurium	H_2Te	–	–1	Very unstable, unlikely to be important, toxic, highly flammable, pungent odour, explosive air mixture
	Alkylated Te compounds	–	–	Microbial action
Tin	Stannane, SnH_4			
	Alkylated tin compounds			Disposal and microbial action
Tungsten, molybdenum and possibly some other transition metals	Metal carbonyls			From reaction between metal in an active form and CO, probably via microbial action. Nickel carbonyl mentioned above. Only Fe, Cr and V carbonyls likely to be stable. No evidence from existing landfills
Indium, Thallium, Cadmium, Zinc				Methylated compounds? Possible for Cd. No data yet found for others from landfills.

5.2 Trace gases

The trace gases in Table 5.2 can arise from chemical or microbial reactions, although in some cases the mechanism of production is not known. They can be conveniently grouped into three classes:

- **Generated by chemical reaction:** H_2S (from sulphides), H_2Se, HSCN, HCN, SbH_3, AsH_3, simple hydrocarbons (from carbides), HCl etc., Hg, NH_3, N_yO_x, PH_3, H_2Se, $COCl_2$ (and, potentially, under some circumstances I_2, Br_2, Cl_2, F_2, SO_2).
- **Generated by microbial action:** H_2S (from sulphate), R_2S, SbH_3, SbR_3, AsH_3, AsR_3, BiR_3, CO, CS_2, COS, (and, possibly, the selenium analogues CSe_2 and COSe), simple hydrocarbons, organic acids, PbR_4, Hg, HgR_2, NH_3, N_yO_x, PH_3, H_2Se, R_2Se, R_2Te, SnR_4 (R = alkyl groups including methyl and, in this context only, partially substituted with R = H in some cases) and, potentially, alkylated species of other metals.
- **Generation mechanism uncertain (possibly combination of microbial and chemical):** $Ni(CO)_4$, $W(CO)_6$, $Mo(CO)_6$ and, possibly, other transition metal carbonyls.

Several of these compounds (e.g. mercury, carbon disulphide) may also occur as 'as-disposed' contaminants in wastes. Some volatile inorganic stable species such as NF_3, SF_6 and siloxanes are only likely to occur if they are present in the wastes at the time of disposal. Other species such as the halogens and hydrogen halides are so reactive that, if traces are formed by reaction in a landfill cell, they are likely to react with other waste components (e.g. iron and steel) provided their residence time allows a suitable amount of mixing (i.e. they are not swept out rapidly in bulk gas).

Appendix A of the *Guidance on the Management of Landfill Gas* (Environment Agency 2004a) gives an extensive list of the trace components (about 500) that have been identified in landfill gas. The vast majority of these are organic compounds but the following inorganic or organo-metalloid species are listed:

- arsenic
- carbon disulphide
- carbon monoxide
- carbonyl sulphide
- dimethyl disulphide
- dimethyl sulphide (and a number of other alkylated sulphides[4])
- hydrogen
- hydrogen chloride
- hydrogen cyanide

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[4] Dibutyl sulphide, dibutyl trisulphide, diethyl disulphide, diethyl sulphide, dimethyl tetrasulphide, dimethyl trisulphide, dipropyl sulphide, ethyl isopropyl disulphide, ethyl *n*-propyl disulphide, ethyl isobutyl disulphide, ethylmethyl disulphide, ethylmethyl trisulphide, ethylpropyl disulphide, ethylpropyl trisulphide, methyl butyl disulphide, methyl isopropyl disulphide, methyl propyl disulphide, methyl ethyl sulphide, methyl propyl trisulphide, *n*-butyl disulphide, propyl butyl disulphide.

- hydrogen fluoride
- hydrogen sulphide
- mercury
- sulphur dioxide
- sulphuric acid.

Landfill gas sampling campaigns have been carried out as part of the Environment Agency's R&D programme (Environment Agency 2002a, 2003b). Gas samples were taken in 2002 and 2003 from six different types of landfills accepting predominantly MSW. The chosen sites had either each taken a proportion of other wastes that may affect the trace component composition [e.g. fragmentiser waste, co-disposed wastes, ash or commercial & industrial (C&I)] or represented different waste management regimes.

Samples were taken from the main gas extraction supply at each site. In addition, samples were taken at three sites from different locations:

- recent waste monitoring well;
- leachate well;
- mature waste monitoring well.

Although the work was concerned primarily with trace organic species in landfill gas, analyses were also undertaken for:

- volatile total arsenic (unspeciated);
- hydrogen sulphide;
- carbon disulphide
- dimethyl sulphide (other organosulphur species were also analysed).

These gases are among those identified in Table 5.2 as potentially present as traces in gas from inorganic waste landfills. Although all the sites had taken biodegradable waste, a comparison of the results provides some information on these gases relevant to inorganic landfills.

The mean arsenic concentrations found in the 2003 sampling campaign were between 0.6 and 409.5 µg m^{-3} (see Table 5.3). The highest arsenic concentrations were found in gas from recent waste (409.5 µg m^{-3}) and leachate (117.2 µg m^{-3}) from a site taking waste with 'substantial ash'. This would suggest that the combination of arsenic in an available form in the ash, coupled with microbial activity arising from the biodegradable waste, leads to the volatilisation of arsenic. In contrast, the arsenic concentration in gas from mature waste at this site was much lower at 1.6 µg m^{-3} and this could suggest that the peak generation rate of volatile arsenic occurs relatively soon after disposal.

A similar trend is seen for the gas from the C&I site, although the arsenic concentrations are much lower [5.5 µg m^{-3} (recent waste), 11 µg m^{-3} (leachate) and 0.6 µg m^{-3} (mature waste)] and the main gas contains the highest arsenic concentration (34.3 µg m^{-3}). The 'substantial ash' site accepts mainly C&I waste in conjunction with the ash, which was generated by an incinerator plant formerly located on-site. However, it may be unwise to draw firm conclusions from this limited dataset as the highest arsenic concentration in gas from the 'mainly domestic with leachate' site was found in mature waste (43.9 µg m^{-3}).

Table 5.3 Mean total arsenic concentrations in gas samples taken from six types of landfill in 2003[1]

Type of landfill[2]	Total concentration of arsenic in gas sample (µg m^{-3})			
	Main gas	**Recent waste**	**Leachate**	**Mature waste**
Co-disposal	3.1	–	–	–
Mainly domestic (with leachate)	28.7	3.7	4.9	43.9
Mainly domestic (little leachate)	4.2	–	–	–
Substantial ash	31.5	409.5	117.2	1.6
Substantial fragmentiser waste	6.8	–	–	–
Commercial and industrial (C&I) (non-hazardous)	34.3	5.5	11.0	0.6

Notes: [1] Environment Agency (2003b)
[2] All sites contain biodegradable waste

Table 5.4 shows that hydrogen sulphide concentrations were in the range 2,400 to 580,000 µg m^{-3}. For the three types of landfill where samples were taken from four locations (main gas, recent waste, leachate and mature waste), the concentrations were higher in gas from recent waste than in gas from the mature waste. The hydrogen sulphide concentrations in the main gas from all six sites were within a narrower range of 31,000 to 110,000 µg m^{-3} (although the gas from the site taking waste with a 'substantial fragmentiser' content was quantified at >67,000 µg m^{-3}).

In a similar manner to hydrogen sulphide, the concentrations of carbon disulphide were always higher in gas from recent waste than in gas from the mature waste for the three types of landfill where such samples were taken. Comparison of all the data from the six sites in Table 5.4 shows the carbon disulphide concentrations to be in the range 900 to 170,000 $µgm^{-3}$.

Table 5.4 Mean concentrations (µg m^{-3}) of hydrogen sulphide, carbon disulphide and dimethyl disulphide in gas samples taken from six types of landfill in 2003[1]

Species	Type of landfill[2]					
	C&I (non-hazardous)	**Mainly domestic (little leachate)**	**Mainly domestic (with leachate)**	**Co-disposal**	**Substantial fragmentiser waste**	**Substantial ash**
Main gas						
H_2S	110,000	49,000	31,000	52,000	>67,000	53,000
CS_2	59,000	32,000	170,000	1,650	1,400	2,600
$(CH_3)_2S_2$	170	170	70	150	<30	480
Recent waste						
H_2S	200,000	–	300,000	–	–	>69,000
CS_2	18,000	–	87,000	–	–	35,000
$(CH_3)_2S_2$	30	–	790	–	–	12,000
Leachate						
H_2S	53,000	–	580,000	–	–	>68,000
CS_2	7,000	–	68,000	–	–	13,000
$(CH_3)_2S_2$	60	–	180	–	–	960
Mature waste						
H_2S	2,400	–	25,000	–	–	7,000
CS_2	1,400	–	12,800	–	–	900
$(CH_3)_2S_2$	<30	–	70	–	–	170

Notes:
[1] Environment Agency (2003b)
[2] All sites contain biodegradable waste

Dimethyl disulphide (70–480 µg m^{-3}) was detected at every main gas sampling location apart from the site taking ‘substantial fragmentiser’ waste (<30 µg m^{-3}). Higher concentrations of dimethyl disulphide were typically sampled from recent waste than from mature waste at the ‘mainly domestic (with leachate)’, ‘substantial ash’ and C&I sites.

Tables 5.5 and 5.6 list important compounds in landfill gas in terms of toxicological and odour importance respectively (Environment Agency 2003b). Inorganic and methylated species of relevance to the discussion above are highlighted in bold. These are:

- arsenic and mercury for toxicity;
- dimethyl disulphide and dimethyl sulphide for odour;
- hydrogen sulphide and carbon disulphide for toxicity and odour.

Table 5.7 summarises the trace compounds likely to be generated by chemical or microbial reactions within a mixed hazardous landfill or a mixed non-hazardous landfill. It identifies qualitatively whether the compounds are likely to be hazardous in terms of their toxicity, flammability and their ability to form explosive mixtures in air; it also notes whether the compound could be an issue in terms of odour. These considerations are based on various sources of data on laboratory hazards and, if no data are available, reasonable judgement where this is possible. Table 5.7 also indicates:

- the likely type of generation (microbial, chemical) and whether anoxic conditions may be required;
- the likely stability within the landfill (thermal stability, reactivity with water and other materials within the landfill) and whether oxic conditions would affect stability (see Appendix C);
- the likely stability above the landfill (thermal stability, reactivity with water, reactivity in air, photolytic degradation).

Hirner (2003) identified that two of the conditions favouring biomethylation were metal(loid)s in easily accessible forms (e.g. as ions) and the presence of microorganisms with biomethylation potential (see Section 4.3.2). This implies that:

- water must be available (i.e. the wastes must be damp);
- the appropriate microorganisms must be present as an active population.

For the reasons discussed in Section 3.3.1, microbial action is likely to occur in niches where conditions are most favourable. This would tend to spread the generation of methylated species over a longer period of time than if microbial action occurred throughout the landfill. In some waste types, the element of concern may not be reasonably accessible. Thus, as discussed in Section 4.3.3, the generation of phosphine from steels depends on the rate of corrosion and the inventory of phosphorus in steel is not instantly available for release as phosphine. Similarly, elements such as arsenic, antimony and selenium in waste electronic components may not be readily available immediately after landfilling. Conversely, a process such as incineration will increase the concentration of some elements in the ash or pollution control residues, relative to the initial waste feed, and may also render them more accessible.

Table 5.5 Concentrations of top 16 toxicity priority trace components in landfill gas[1,2,3]

Species	**Average concentration from sites sampled in R&D Project P1-491 [1] (10^{-6} g m^{-3})**	**Average concentration from Environment Agency's historic database [2,] (10^{-6} g m^{-3})**
Chloroethene	1.02×10^5	6.63×10^4
Benzene	1.84×10^4	4.86×10^3
Chloroethane	4.61×10^2	7.68×10^4
2-butoxy ethanol	$\leq 2.0 \times 10^2$	2.00×10^2
Arsenic	5.11×10^1	3.65×10^0
Trichloroethene	8.59×10^3	1.50×10^4
1,1-dichloroethene	2.23×10^3	1.00×10^2
Furan	1.43×10^3	9.75×10^2
Hydrogen sulphide	1.33×10^5	1.34×10^5
1,1-dichloroethane	5.64×10^2	4.77×10^5
Carbon disulphide	3.40×10^4	7.66×10^1
1,2-dichloroethene	6.15×10^3	1.65×10^4
Tetrachloromethane	$\leq 7.0 \times 10^1$	5.26×10^3
Methanal	5.90×10^1	2.93×10^3
1,3-butadiene	$\leq 7.0 \times 10^1$	1.82×10^2
Mercury	5.00×10^{-1}	4.09×10^0

Notes:

[1] Environment Agency (2003b)
[2] Environment Agency (2002a)
[3.] Bold entries = inorganic, organometalloid species

Table 5.6 Concentrations of top 16 odorous priority trace components in landfill gas[1,2,3]

Species	Average concentration from sites sampled in R&D Project P1-491 [1] (10^{-6} g m^{-3})	Average concentration from Environment Agency's historic database [2,] (10^{-6} g m^{-3})
Hydrogen sulphide	1.33×10^5	1.34×10^5
Methanethiol	$\leq 1.0 \times 10^3$	7.26×10^3
Carbon disulphide	3.40×10^4	7.66×10^1
Butyric acid	1.75×10^3	8.96×10^3
Dimethyl disulphide	1.19×10^3	2.15×10^2
Ethanal	3.91×10^2	2.93×10^3
Ethanethiol	$\leq 3.0 \times 10^2$)	1.45×10^2
1-pentene	5.49×10^3	1.72×10^3
ethyl butyrate	7.24×10^3	3.29×10^4
Dimethyl sulphide	$\leq 1.1 \times 10^2$	4.80×10^2
1-butanethiol	$\leq 1.1 \times 10^2$	2.00×10^2
1-propanethiol	6.00×10^0	4.33×10^2

Notes:
[1] Environment Agency (2003b)
[2] Environment Agency (2002a)
[3.] Bold entries = inorganic, organometalloid species

Table 5.7 Gaseous trace species likely to be generated in inorganic landfills[1]

Species	Toxic?	Flammable?	Unpleasant oOdour?	Explosive mixture with air?	Typical concentration[2] in gas from existing landfills (or other experiments[3]) ($g\ m^{-3}$)	Potential generation process	Anaerobic conditions required[4]?	Comments on stability within landfill	Stable if conditions oxic?	Comments on stability in atmosphere above landfill	Stable in air + light?
Group VIa											
$Mo(CO)_6$	Y	N	N	N	1×10^{-8} to 3×10^{-7} (Feldmann and Cullen 1997)	Possibly chemical, probably microbial, needs CO	Y	Relatively stable	Y	Relatively stable, possibly photochemically unstable	N?
$W(CO)_6$	Y	N	N	N	5×10^{-9} to 2×10^{-7} (Feldmann and Cullen 1997)	Possibly chemical, probably microbial, needs CO	Y	Relatively stable	Y	Relatively stable, possibly photochemically unstable	N?
Group VIII											
$Ni(CO)_4$	Y	Y	Y	Y	(5×10^{-7} To 1×10^{-6})*** (Feldmann 1999)	Chemical/ microbial, needs CO	Y	Highly reactive	N	Highly reactive	N
Group IIb											
Hg^0	Y	N	N	N	9×10^{-7} (Feldmann 2003) 1×10^{-8} to 1×10^{-5} (Lindberg *et al.* 2005)	'as disposed', demethylation	N	Stable	Y	Stable	Y
$Hg(CH_3)_2$	Y	Y	N	N	1×10^{-7} (Feldmann 2003) 5×10^{-9} to 8×10^{-8} (Lindberg *et al.* 2005)	Microbial	Y	Stable	?	Decomposes to monomethyl Hg	N?
$(CH_3)Hg^+X^-$ (expected X = OH or Cl)	Y	Y?	N?	N?	2×10^{-9} to 4×10^{-8} (Lindberg *et al.* 2005)	Microbial	Y	?	?	?	?

Table 5.7 (cont'd) Gaseous trace species likely to be generated in inorganic landfills[1]

Species	Toxic?	Flammable?	Unpleasant odour?	Explosive mixture with air?	Typical concentration[2] in gas from existing landfills (or other experiments[3]) (g m^{-3})	Potential generation process	Anaerobic conditions required[4]?	Comments on stability within landfill	Stable if conditions oxic?	Comments on stability in atmosphere above landfill	Stable in air + light?
Group IVb											
Simple hydrocarbons excluding methane (acetylene used as example)	N	Y	N	Y		Chemical (carbides)	N	Stable	Y	Stable	Y
CO	Y	Y	N	Y	6×10^{-3} (median) (Environment Agency 2004a)	Chemical, thermal	Y	Stable	Y	Stable	Y
$COCl_2$	Y	N	Y	N	–	Chemical	N	Decomposes on contact with water to give CO and HCl	N	Decomposes on contact with water to give CO and HCl	N
HCN	Y	Y	Y	Y	–	Chemical	N	Stable	Y	Stable	Y
Si? Ge?											
$(CH_3)_4Sn$	Y	Y	–	–	1×10^{-4} (Feldmann 2003)	Microbial	Y	Hydrolyses?	N?	Decomposed by light in air?	N?
Other alkylated tin compounds (unknown)	Y?	–	–	–	3×10^{-5} (Feldmann 2003)	'As disposed?', microbial	Y	Some relatively stable?	Y?	Decomposed by light in air?	N?
$Pb(CH_3)_4$	Y	Y	Y	Y	'ng per m^3 range' (Feldmann and Cullen 1997)	Microbial	Y	Hydrolyses?	?	Light sensitive?	N?
$Pb(CH_3)(C_2H_5)_3$	Y	Y?	Y?	Y?	4×10^{-8} (Feldmann 2003)	Microbial	Y	Hydrolyses?	?	Light sensitive?	N?
$Pb(C_2H_5)_4$	Y	Y	Y	Y	1×10^{-6} (Feldmann 2003) 'ng per m^3 range' (Feldmann and Cullen 1997)	'As disposed?', microbial	Y	Hydrolyses?	Y	Light sensitive	N

Table 5.7 (cont'd) Gaseous trace species likely to be generated in inorganic landfills[1]

Species	Toxic?	Flammable?	Unpleasant odour?	Explosive mixture with air?	Typical concentration[2] in gas from existing landfills (or other experiments[3]) (g m^{-3})	Potential generation process	Anaerobic conditions required[4]?	Comments on stability within landfill	Stable if conditions oxic?	Comments on stability in atmosphere above landfill	Stable in air + light?
Group Vb											
NOx (for NO_2)	Y	N	Y	N	–	Chemical	N	Reactive, dissolves to give nitric acid	Y	Reactive	Y
NH_3	Y	Y	Y	Y	–	Chemical, microbial	Y	Highly water soluble	Y	Stable	Y
Amines (for example of trimethylamine)	Y	Y	Y	Y	–	Chemical, (microbial from putrescibles)	N	Water soluble	–	Probably not persistent in environment	N
PH_3	Y	Y	Y	Y	3×10^{-6} to 3×10^{-7} (Roels and Verstraete 2004)	Microbial, chemical. Odour at low concentrations due to impurities	Y	Pyrophoric, spontaneously flammable in air due to impurities	N	Pyrophoric, spontaneously flammable in air due to impurities	N
AsH_3	Y	Y	Y	Y	7×10^{-8} (Feldmann 2003)	Microbial, chemical	Y	Thermally unstable, pyrophoric	N	Thermally unstable, pyrophoric	N
CH_3AsH_2	Y?		Y?		4×10^{-6} (Feldmann 2003)	Microbial	Y	–	–	Decomposed by light in air	N
$(CH_3)_2AsH$	Y?		Y?		1×10^{-8} (Feldmann 2003)	Microbial	Y	–	–	Decomposed by light in air	N
$(CH_3)_3As$	Y		Y		4×10^{-6} (Feldmann 2003)	Microbial	Y	–	–	Decomposed by light in air	N

Table 5.7 (cont'd) Gaseous trace species likely to be generated in inorganic landfills[1]

Species	**Toxic?**	**Flammable?**	**Unpleasant odour?**	**Explosive mixture with air?**	**Typical concentration[2] in gas from existing landfills (or other experiments[3]) (g m^{-3})**	**Potential generation process**	**Anaerobic conditions required[4]?**	**Comments on stability within landfill**	**Stable if conditions oxic?**	**Comments on stability in atmosphere above landfill**	**Stable in air + light?**
$(CH_3)_2As(C_2H_5)$	Y		Y?		4×10^{-8} (Feldmann 2003)	Microbial	Y	–	–	Decomposed by light in air?	N?
$As(C_2H_5)_3$	Y		Y?		–	Microbial	Y	–	–	Decomposed by light in air?	N?
Total volatile arsenic (unspeciated)	Y?	–	–	–	6×10^{-7} to 4×10^{-4} (Environment Agency 2003b)	–	–	–	–	–	–
$(CH_3)_3Sb$	Y?				1×10^{-4} (Feldmann, 2003) (2×10^{-4})** (Michalke *et al.* 2000)	Microbial	Y	–	–	Decomposed by light in air	N
SbH_3	Y	Y	Y	Y	(2×10^{-4})** (Michalke *et al.* 2000)	Microbial action, chemical action	Y	Reacts with moisture	–	Decomposed by light in air	N
$(CH_3)_2SbH$	Y?				(2×10^{-5})** (Michalke *et al.* 2000)	Microbial	Y	Possibly intermediate to $(CH_3)_3Sb$?	N	Decomposed by light in air	N
$(CH_3)SbH_2$	Y?				(2×10^{-5})** (Michalke *et al.* 2000)	Microbial	Y	Possibly intermediate to $(CH_3)_3Sb$?	N	Decomposed by light in air	N
$(CH_3)_3Bi$					1×10^{-6} (Feldmann 2003) (4×10^{-5} to 1×10^{-4})** (Michalke *et al.* 2000)	Microbial	Y	–	–	–	–

Table 5.7 (cont'd) Gaseous trace species likely to be generated in inorganic landfills[1]

Species	Toxic?	Flammable?	Unpleasant odour?	Explosive mixture with air?	Typical concentration[2] in gas from existing landfills (or other experiments[3]) ($g\ m^{-3}$)	Potential generation process	Anaerobic conditions required[4]?	Comments on stability within landfill	Stable if conditions oxic?	Comments on stability in atmosphere above landfill	Stable in air + light?
GroupVIb											
H_2S	Y	Y	Y	Y	3×10^{-2} to 6×10^{-1} (Environment Agency 2003b)*	Microbial, chemical.	Y/N	Soluble	Y	–	Y
CS_2	Y	Y	Y	Y	1×10^{-3} to 2×10^{-1} (Environment Agency 2003b)*	'As disposed?', microbial				Decomposes in sunlight	N
COS	Y	Y	Y	Y	–	'As disposed?', microbial	–	Corrosive to common metals with water present	–	–	–
$(CH_3)_2S_2$	Y	Y	Y	N?	$<3 \times 10^{-5}$ to 1×10^{-2} (Environment Agency 2003b)*	Microbial	Y	–	N?	Probably oxidises	N?
CH_3SH	Y	Y	Y	?	33 to 22,550 ppb (Kim *et al.* 2005)	Microbial	Y	Soluble	Y?	Probably oxidises	N?
$(CH_3)_2S$	Y	Y	Y	Y?	33 to 7,120 ppb (Kim *et al.* 2005)	Microbial	Y	–	N?	Probably oxidises	N?
$(CH_3)_2Se$	Y	N	Y	N	(6×10^{-5})** (Michalke *et al.* 2000)	Microbial	Y	Reacts with water	–	–	–
H_2Se	Y	Y	Y	Y	-	Microbial, chemical	Y/N	Reacts with water	–	–	–
$(CH_3)_2Se_2$	Y?		Y?		2×10^{-8} (Feldmann 2003) (3×10^{-4})** (Michalke *et al.* 2000)	Microbial	Y	–	-	–	–
CSe_2	Y	N	Y?	N	-	Microbial	–	–	–	–	–
$(CH_3)_2Te$	Y		Y		1×10^{-7} (Feldmann 2003) (3×10^{-6})** (Michalke *et al.* 2000)	Microbial	Y	Thermally unstable, reacts with H_2O and air	N	Thermally unstable, reacts with H_2O and air	N

Table 5.7 (cont'd) Gaseous trace species likely to be generated in inorganic landfills[1]

Species	Toxic?	Flammable?	Unpleasant odour?	Explosive mixture with air?	Typical concentration[2] in gas from existing landfills (or other experiments[3]) (g m^{-3})	Potential generation process	Anaerobic conditions required[4]?	Comments on stability within landfill	Stable if conditions oxic?	Comments on stability in atmosphere above landfill	Stable in air + light?
Group VIIb											
Hydrogen halides	Y HF HCl	N	–	N	–	Chemical	N	Highly reactive, water soluble	Y	Highly reactive, water soluble	Y
CH_3I	Y	N	Y	N	–	Microbial	–	Decomposes in presence of moisture	–	Decomposes in presence of light and moisture	N

Notes:

[1] N = No, Y = Yes based on data from various sources, Y? or N? = Yes or No based on judgement by analogy with similar compounds, – = not possible to make a judgement (or, for mixed species, not applicable).

[2] Concentrations as the elements unless otherwise noted by * (* = concentration of molecular species)

[3] (Other experiments) denoted in ( ) are for gas samples taken from above incubated sewage sludge or *M. formicicum* cultures in laboratory experiments** ,or gas sampled from sewage treatment plants***

[4] Anaerobic conditions may be required on at least the point of generation (e.g. arsine). Some methylation has been detected under aerobic conditions but in general seems more favoured under anaerobic conditions (i.e. methanogenic conditions).

5.3 Trace gases from ‘as-deposited’ material

Any volatile material present in the solid waste when it is deposited is likely to enter the gas phase as a trace component. These substances will be partitioned between the liquid, solid and gas phases; conditions in the landfill will affect the quantity and rate at which they are released.

Fugacity models such as MOCLA have been used to model and predict the partitioning of organic molecules in MSW landfill (Kjeldsen and Christensen 2001). Similar principles would apply in an inorganic landfill. However, it is likely that pre-treatment will have lowered the amounts of volatile substances present in predominantly inorganic wastes and so the quantities of trace substances will be low. But since the volume of bulk gas will be much lower than at an MSW landfill, the concentration of these traces may not necessarily be lower.

6 Calculation of hydrogen generation rates and redox evolution

The redox conditions in a landfill containing metal residues will affect the gas generation processes. Hydrogen generation will be an important determinant of whether a landfill is anaerobic since hydrogen is the bulk gas most likely to displace the initial inventory of air from the landfill and will balance the slow ingress of air into the waste through the engineered barriers.

Scoping calculations were performed in order to investigate the effect of metal corrosion on the evolution of the redox conditions of a landfill facility and the potential for hydrogen gas production. Two types of calculation were performed:

- for an unsaturated landfill facility filled with waste and initially aerobic;
- for a saturated landfill facility filled with waste and initially aerobic.

A number of assumptions were required for each calculation. These and the methodology used are discussed in Appendix D. In all cases, the calculations relate to the period after emplacement of the waste and capping of the landfill cell. No allowance is made for displacement of oxygen by any gases produced in the landfill.

6.1 Unsaturated landfill facility

The first step in the calculations was to predict whether the landfill facility would become anaerobic based on the assumptions and starting conditions using the methodology described in Appendix D. This will occur when the rate of oxygen consumption due to the aerobic corrosion of mild steel is much greater than the rate of oxygen ingress. An example of the values of the parameters used and the calculated rates and steady state partial pressure of oxygen are given in Table 6.1.

In the second step the rate of hydrogen generation is calculated. An example of the set of parameter values used for the unsaturated calculations is given in Tables 6.2 and 6.3. For cases where the oxygen in the landfill is consumed, mild steel corrosion can continue anaerobically (at a different rate to aerobic corrosion). This process generates hydrogen. Reaction of other reactive metals in the waste might also lead to hydrogen evolution, even under aerobic conditions.

From an estimation of the masses of steel, aluminium and zinc in the waste and reported corrosion rate data (ASM 1987, Smart 2002), the amount of hydrogen generated can be calculated. It has been assumed that the corrosion rates of aluminium and zinc, and the anaerobic corrosion rate of mild steel are not time dependent – except that the latter occurs only once anaerobic conditions have been established. The data are used to calculate:

- the time until anaerobic conditions are established;
- the hydrogen evolution rate;
- the time until metal exhaustion.

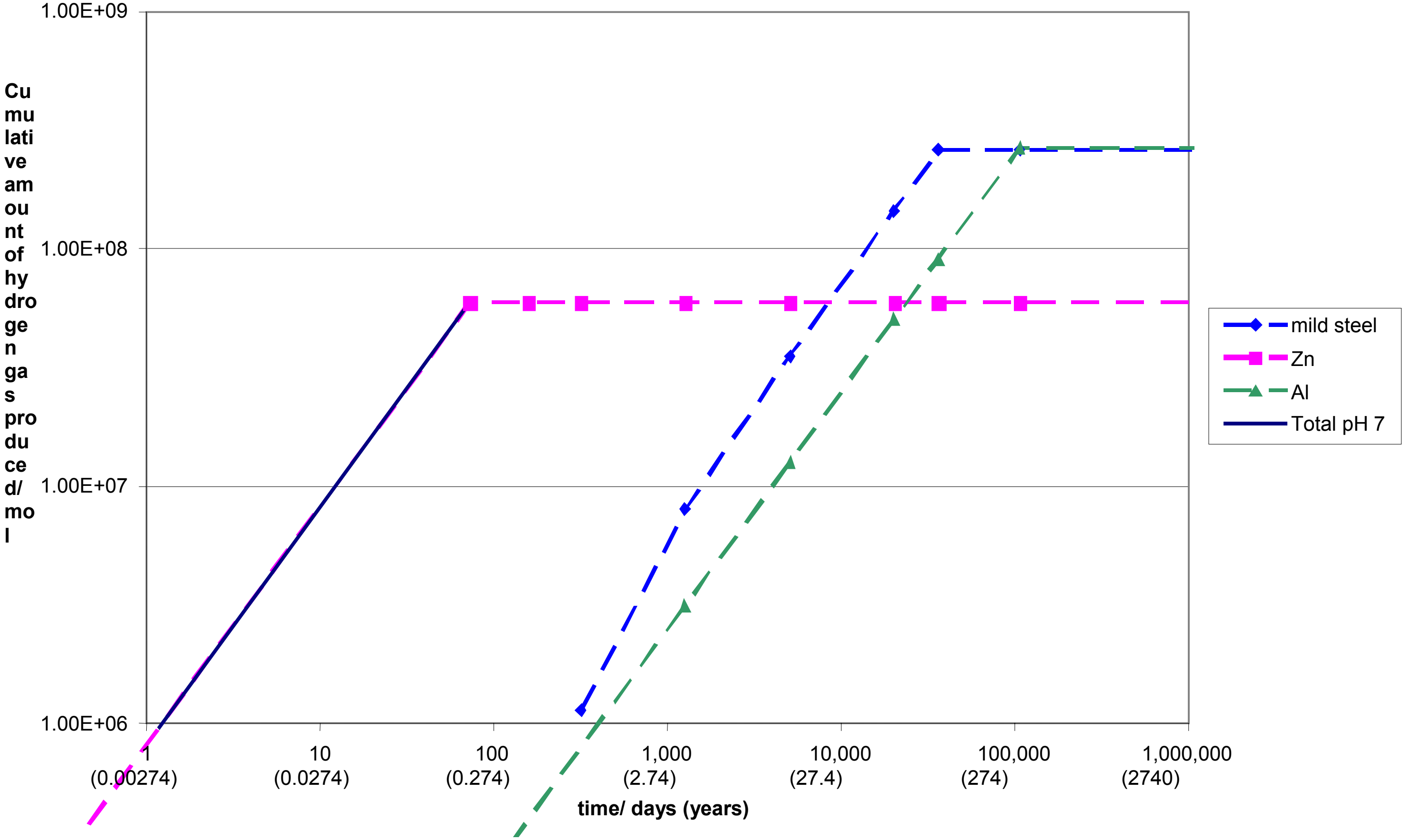
These can be used to calculate the cumulative hydrogen evolution profile as shown, for example, in Figure 6.1.

Table 6.1 Example steady state calculation of the partial pressure of oxygen assuming pH 7 unsaturated conditions[1]

Main calculation (see Section 6.1)			Supporting values and calculations					
Quantity	**Value**	**Units**	**Quantity**	**Value**	**Units**	**Quantity**	**Value**	**Units**
Oxygen ingress								
K_1	2.5 x 10^{-5}	kg s^{-1}	Ingress rate 2)	**0.001**	mg m^{-2} s^{-1}			
				10^{-9}	kg m^{-2} s^{-1}			
			Depth 2)	**40**	m			
			Volume waste 2)	**10^{6}**	m^3			
			Horizontal landfill (cross-sectional area)	25,000	m^2			
Corrosion								
k	3.17 x 10^{-12}	m s^{-1}	Corrosion rate (Smart 2002)	**0.1**	mm $year^{-1}$			
z	3,380	kg m^{-3}	Mass per 1 m^3 steel	7,850	kg m^{-3}	Density (Sutherland 2004)	7,850	kg m^3
			Amount Fe	140,700	mol	Atomic mass Fe	55.8	g mol^{-1}
			Amount O_2 3)	105,500	mol			
			Mass O_2	3,376	kg m^{-3}	Molecular mass O_2	32	g mol^{-1}
K_2	1.07 x10^{-8}	kg m^{-2} s^{-1}						
			Percentage steel in waste 4)	**1.1**				
			Mass waste	**10^{9}**	kg			
			Mass steel	1.1 10^{7}	kg			
A_m	2.81 x10^{6}	m^2	Assumed specific area of steel	**0.255**	m^2 kg^{-1}			
K_2 A_m	0.0	kg s^{-1}						
Steady state								
p_{ss}	1.74 x10^{-4}	atmosphere	p_{atm} (Lide 1994)	0.209	atmosphere			

Notes:

[1] **Bold** values are main input parameters that may be varied.
[2] Professional judgement by A. Rosevear provided as a personal communication.
[3] Assuming conversion of iron to haematite: $4Fe + 3O_2 = 2Fe_2O_3$.
[4] Estimated for hazardous waste landfill (see Section 3.2.1 and Table 3.1)



Calculations were performed using input values indicated in Tables 6.1, 6.2 and D1, and assumptions discussed in Appendix D.

Figure 6.1 Predicted hydrogen evolution profiles for pH 7 unsaturated conditions and a mild steel thickness of 1 mm

6.1.1 Results for unsaturated conditions

The details of the calculations are set out in Tables 6.2 and 6.3 using the pH 7 case as an example. The main results for the range of pH values and mild steel thicknesses considered are summarised in Table 6.4 and Figures 1–4.

For pH 7 and a steel thickness of 1 mm, the results indicate that under the assumed conditions the rate of oxygen ingress is small compared with the rate of consumption by mild steel corrosion. Hence the steady-state partial pressure of oxygen is predicted to fall to 1.74×10^{-4} atmospheres. This value is just below the chosen criterion for anaerobic conditions (partial pressure of oxygen = 0.1 per cent of its initial value, see Appendix D). The implicit assumption is that anaerobic corrosion can proceed at this partial pressure of oxygen and that its rate is not reduced by this level of oxygen.

The time to the onset of anaerobic conditions was calculated to be around 159 days. It should be noted that this result is dependent on the aerobic corrosion rate value selected for mild steel at pH 7 (Smart 2002) and the total area of the mild steel.

The corrosion rate could be an over-estimate.[5] If there is insufficient water available or if it is largely consumed in corrosion processes or by other processes, then the corrosion rate will be expected to drop. The corrosion rate could also be an over-estimate if the chloride concentration in the available water is low or if the ambient temperature is low (the corrosion rate data have generally been determined at temperatures of 20–25°C). Similarly the corrosion rate would be lower if the steel contains a protective coating (e.g. paint) or if the formation of corrosion products limits the rate at which oxygen reaches the corroding surface.

Table 6.2 Example calculation of time taken to achieve anaerobic conditions assuming pH 7 unsaturated conditions[1]

Main calculation			Supporting values and calculations		
Quantity	**Value**	**Units**	**Quantity**	**Value**	**Units**
Initial rate of oxygen consumption (K_2A_m) 2)	0.03	kg s^{-1}			
			Volume of landfill	**1,000,000**	m^3
Volume of gas in landfill (V_{LF})	200,000	m^3	Porosity of waste	**0.2**	
			Molar volume of O_2 at STP[4]	0.02241	m^3 mol^{-1}
			Molar concentration	44.62	mol m^{-3}
			Mass concentration	1.428	kg m^{-3}
Mass concentration of O_2 in air (c_o)	0.298	kg m^{-3}	Fraction of O_2 in air	0.209	
Time until anaerobic (T_{an}) 3)	1.374×10^7	s			
	159	days			

Notes:
[1] **Bold** values are main input parameters that may be varied.
[2] Calculated in Table 6.1.
[3] Calculated from Equation D6, Appendix D.
[4] standard temperature and pressure

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[5] Due to the assumption in Appendix D: Saturated landfill facility, that layers below the top layer contain oxygen-saturated leachate initially.

Table 6.3 Example calculation of rates of metal corrosion and time until metal exhaustion assuming pH 7 anaerobic unsaturated conditions[1]

	Quantity	Calculation	Mild steel	Zinc	Aluminium
(a)	Corrosion rate (mm year^{-1}) 2)		**0.05**	**0.25**	**0.0034**
(b)	Corrosion rate (m s^{-1})		1.584 x10^{-12}	7.92 x 10^{-12}	1.08 x 10^{-13}
(c)	Specific area (m^{2} kg^{-1})		**0.255**	**2.8**	**0.37**
(d)	Percentage metal in waste		**1.1**	**0.39**	**0.48**
(e)	Total mass metal (kg)		1.10 x 10^{7}	3.90 x 10^{6}	4.80 x 10^{6}
(f)	Area of metal (m^{2})	I × (e)	2.81 x 10^{6}	1.09 x 10^{7}	1.78 x 10^{6}
(g)	Volume rate of metal corroded (m^{3} s^{-1})	(b) × (f)	4.44 x 10^{-7}	8.65 x 10^{-5}	1.91 x 10^{-7}
(h)	Density of metal (kg m^{-3})		7,850	7,140	2,700
(i)	Atomic mass (kg mol^{-1})		0.0558	0.06538	0.02698
(j)	Amount rate of metal corroded (mol s^{-1})	(g) × (h)/(i)	0.0625	9.45	0.0191
(k)	H_2: metal molar ratio		1.333	1	1.5
(l)	Rate of H_2 generation from metal (mol s^{-1})	(j) × (k)	0.0834	9.447	0.0287
(m)	Time to metal consumption (s)	(e)/(i) × (j)	3.13 x 10^{9}	6.31 x 10^{6}	9.29 x 10^{9}

Notes:

[1] **Bold** values are main input parameters that may be varied.

[2] Taken from or estimated from Smart (2002) for steel, ASM (1987) for zinc, and Pryor and Keir (1958) for aluminium.

The calculation of the overall rate of hydrogen evolution requires corrosion rate data for aluminium and zinc as well as for the anaerobic corrosion of mild steel. These have been estimated from graphical data for zinc (ASM 1987) and aluminium (Pryor and Keir 1958). In the case of zinc, the corrosion rate goes through a minimum at around pH 10. At pH 7 and 12, the corrosion rate values for zinc are similar to each other and, at more extreme pH values, the corrosion rate becomes increasingly rapid. For aluminium, the corrosion rate is low in the range pH 4 to 8, but increases rapidly outside this region. At pH 12. aluminium corrosion is rapid. All the corrosion rate data used in this study are shown in Table 6.4.

Table 6.4 summarises the calculation of the relevant hydrogen evolution rates for pH 7 and unsaturated conditions. From these data, the hydrogen evolution profiles are readily calculated as shown in Figure 6.1. The hydrogen evolution due to mild steel corrosion is delayed until anaerobic conditions are achieved. The total hydrogen produced by mild steel corrosion and aluminium are greater than for that for zinc because of their higher loading in the waste. Due to the low corrosion rate for aluminium at pH 7, this metal is the last to be exhausted.

6.1.2 Effect of metal surface areas

The rate of corrosion of all the metals considered is proportional to the available surface area of the metal. Therefore, it depends on both the amount of metal in the waste and the specific surface area. The effect of varying the specific area of the corroding mild steel has been investigated by repeating the calculations at values of 0.255 m^{2} kg^{-1} and 0.0127 m^{2} kg^{-1}. These values correspond to steel thicknesses of 1 mm and 20 mm respectively, selected to approximately represent steel panels and steel girders respectively (alternatively the 0.0127 m^{2} kg^{-1} calculation represents that for 1 mm thick steel in a situation where only 5 per cent of the surface is available for corrosion).

The effects on the steady state partial pressure of oxygen are shown in Table 6.4. For the thick mild steel case (low surface area), the steady-state partial pressure of oxygen is predicted to fall to only 3.44×10^{-3} atmospheres and is not considered to be anaerobic by the criteria specified above. Under these conditions, the hydrogen evolution profile is dependent only on the corrosion of aluminium and zinc as shown in Figure 6.2 because the mild steel corrosion is assumed to proceed aerobically (the total hydrogen generation curve for the thin mild steel case is shown for comparison). In reality, the steel present in the waste will be characterised by a range of specific surface areas[6] and these are likely to vary as corrosion proceeds. This is likely to result in the variation of hydrogen evolution rates with time.

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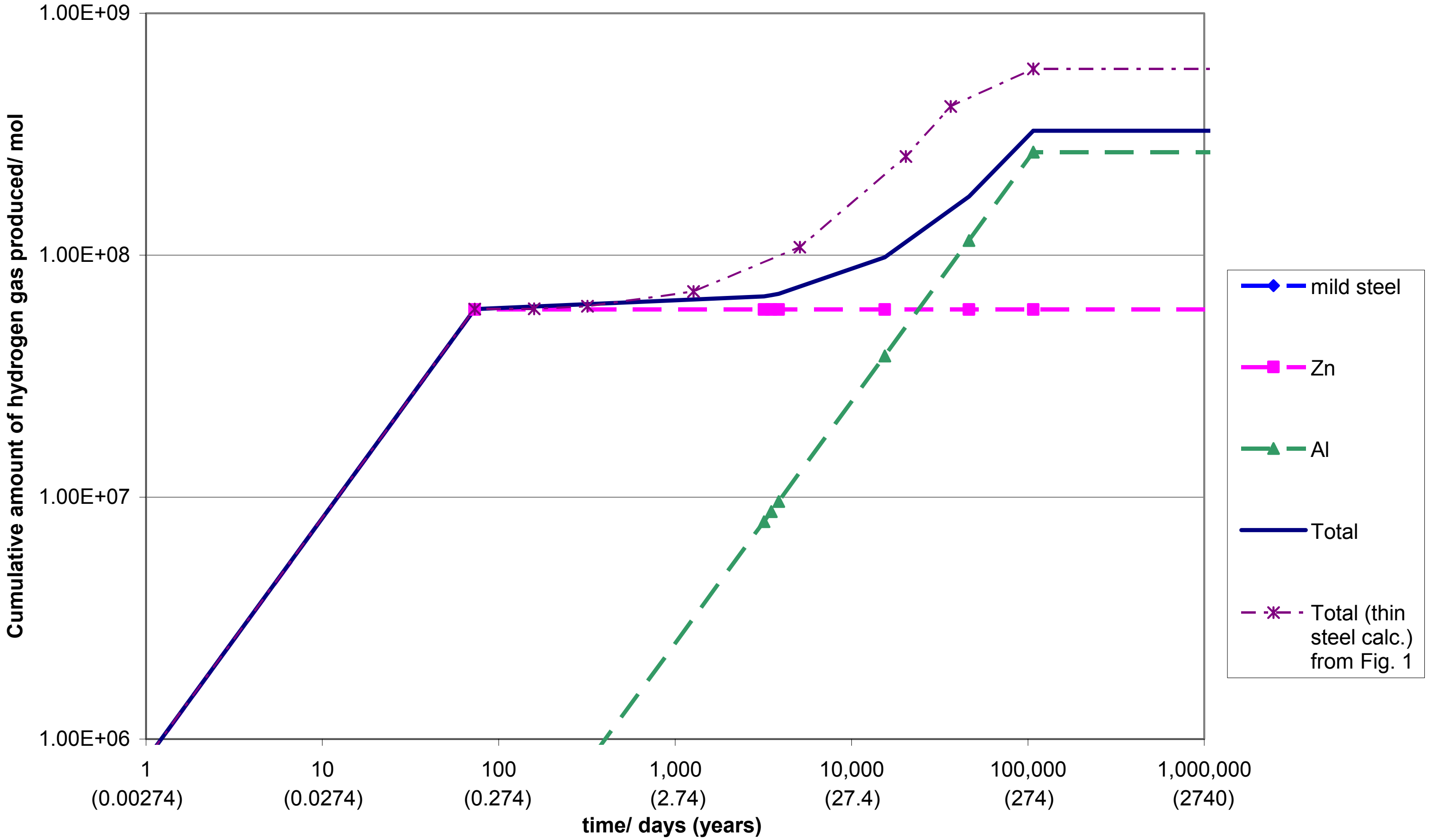
[6] See the assumption in Appendix D: Unsaturated landfill facility, that the specific area of the mild steel in the waste can be represented by a single value that remains constant.



Calculations were performed using input values indicated in Tables 6.1, 6.2 and D1, and assumptions discussed in Appendix D.

Figure 6.2 Predicted hydrogen evolution profiles for pH 7 unsaturated conditions and a mild steel thickness of 20 mm

Table 6.4 Summary of results from calculations under unsaturated conditions

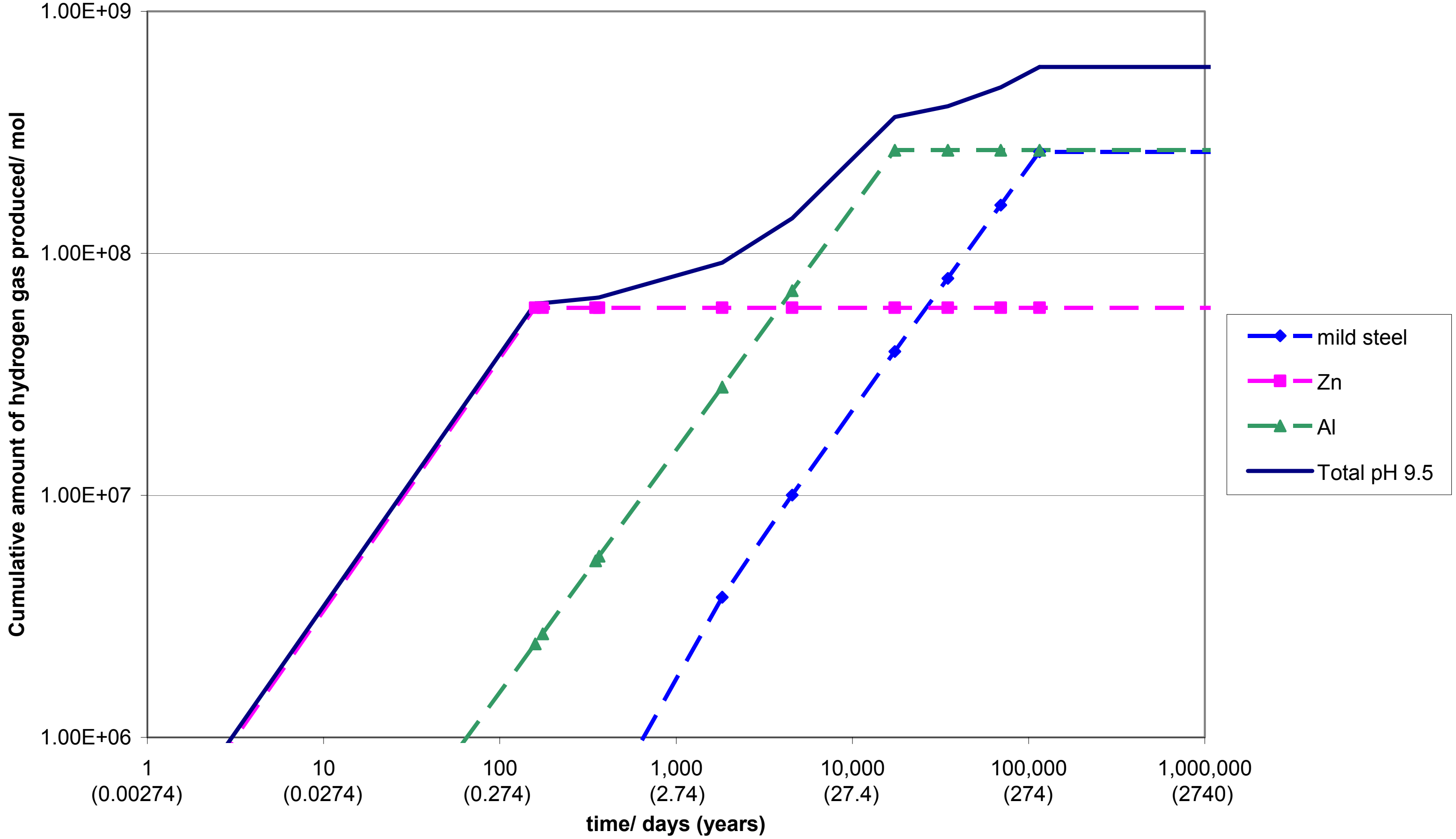
Quantity	Conditions				
	pH 7	**pH 7**	**pH 9.5**	**pH 12**	**pH 7**
	(thick steel, good cap)	**(thin steel, good cap)**			**(thin steel, poor cap)**
Values of varied input parameters					
Mild steel thickness (mm)	20	1	1	1	1
Corrosion rates (mm year^{-1})					
Mild steel (aerobic)	0.1	0.10	0.1	0.1	0.10
Mild steel (anaerobic)	0.005	0.005	0.00158	0.0005	0.005
Zinc	0.25	0.25	0.05	0.25	0.25
Aluminium	0.0034	0.0034	0.021	4.5	0.0034
Results					
Steady state partial pressure of oxygen (atmospheres)	3.44×10^{-3}	1.74×10^{-4}	1.74×10^{-4}	1.74×10^{-4}	1.61×10^{-2}
Time to become anaerobic (days)	Aerobic	159	159	159	Aerobic
Rate of hydrogen production (mol s^{-1})					
Mild steel (anaerobic)	0	0.083	0.026	0.0083	0
Zinc	9.45	9.45	1.89	9.45	9.45
Aluminium	0.029	0.029	0.177	38.02	0.029
Time until metal consumed (days)					
Mild steel	–	36,500	115,000	365,000	–
Zinc	73	73	365	73	73
Aluminium	108,000	108,000	17,400	81	108,000

Table 6.5 Summary of input parameters for numerical simulation of landfill at pH 7 under saturated conditions

Diffusion parameters			Corrosion parameters					
Quantity	**Value**	**Units**	**Quantity**	**Value**	**Units**	**Quantity**	**Value**	**Units**
D 2)	**2×10^{-9}**	$m^2 s^{-1}$	K 3)	0.1	mm $year^{-1}$			
L	**0.1**	m		3.17E-12	m s^{-1}			
L^2	0.01	m^2				Percentage steel in waste [3]	**1.1**	
						Mass of waste [3]	**1.0×10^9**	kg
Δt	**10,000**	s				Mass of steel	1.8×10^7	kg
			A_m	9.0×10^6	m^2	Assumed specific area of steel [3]	**0.255**	$m^2 kg^{-1}$
			Z 3)	3,380	kg m^{-3}			
			V_{LF} 4)	200,000	m^3			

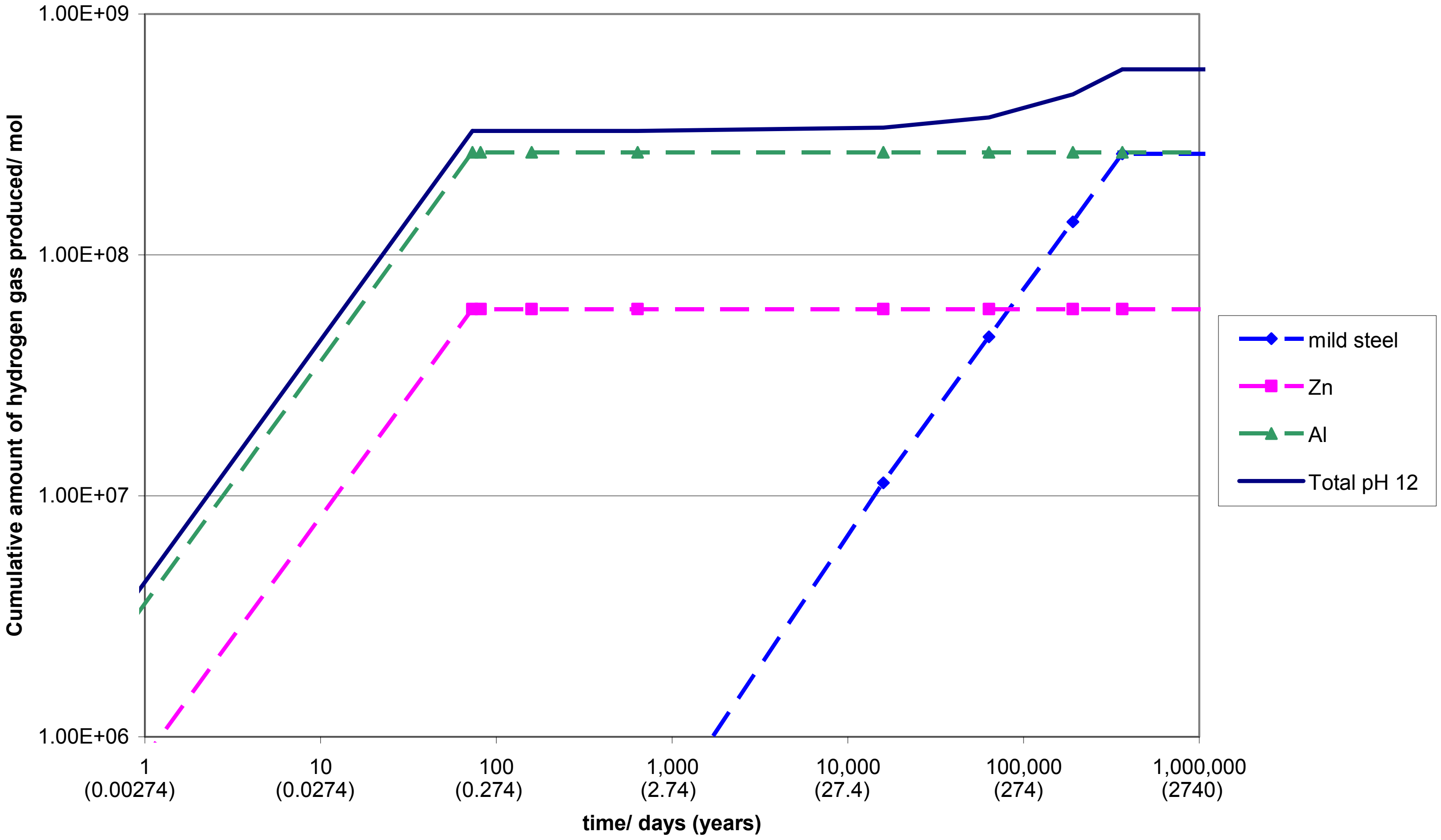
Notes:

[1] **Bold** values are main input parameters that may be varied.
[2] Taken from Tinsley (1979).
[3] Taken from Table 6.1.
[4] Taken from Table 6.2



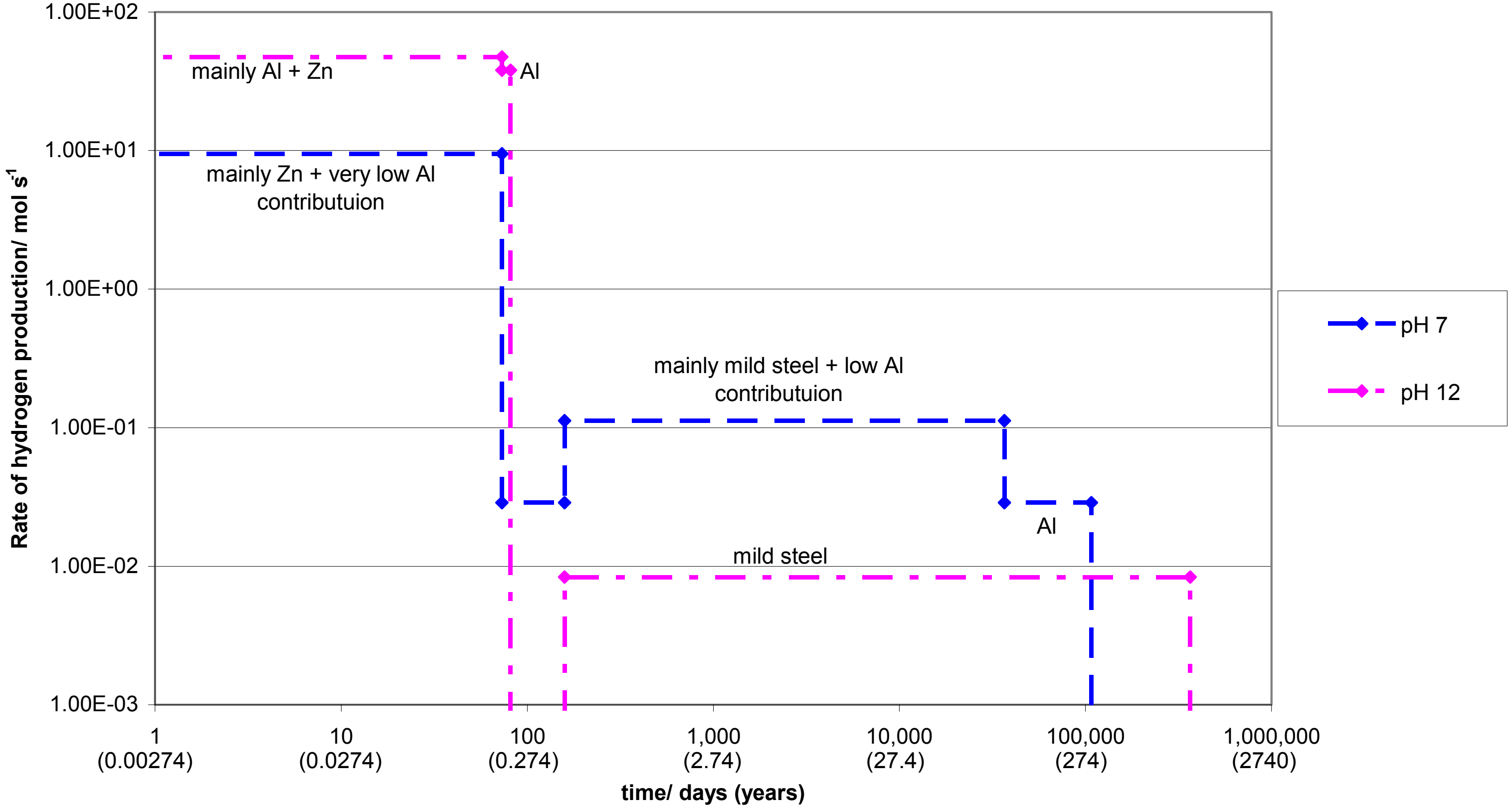
Calculations were performed using input values indicated in Tables 6.1, 6.2 and D1, and assumptions discussed in Appendix D.

Figure 6.3 Predicted hydrogen evolution profiles for pH 9.5 unsaturated conditions and a mild steel thickness of 1 mm



Calculations were performed using input values indicated in Tables 6.1, 6.2 and D1, and assumptions discussed in Appendix D.

Figure 6.4 Predicted hydrogen evolution profiles for pH 12 unsaturated conditions and a mild steel thickness of 1 mm



Calculations were performed using input values indicated in Tables 6.1, 6.2 and D1, and assumptions discussed in Appendix D.

Figure 6.5 Predicted hydrogen evolution rates for unsaturated conditions and a mild steel thickness of 1 mm

6.1.3 Effect of pH

The effect of pH on the landfill environment and hydrogen evolution were also investigated at pH 9.5 and pH 12.5 for the thin mild steel case. The change in pH in the calculations was represented only through the corrosion rates of the mild steel, zinc and aluminium.

In all cases the steady-state partial pressure of oxygen and the time until the onset of anaerobic conditions were the same as for the corresponding pH 7 calculation. This finding results from the use of the same value for the aerobic corrosion rate of mild steel (Smart 2002). The values selected had been used in other modelling work and lie near the centre of the experimental data reviewed by Smart (2002). However, these data show a range of values covering some orders of magnitude in some cases.

At pH 9.5, the early rate of hydrogen production is reduced due to the lower rate of zinc corrosion (Figure 6.3). Similarly the rate from mild steel corrosion is slightly reduced compared with the pH 7 case. The rate of hydrogen production due to aluminium corrosion rises, increasing the total rate of hydrogen production at around 10,000 days.

At pH 12, the aluminium corrosion rate is much greater and leads to rapid hydrogen evolution at early times (Figure 6.4). In contrast, the mild steel corrosion rate and consequent hydrogen evolution rate are significantly slower.

While Figures 6.1–6.4 show the effect of pH on the hydrogen evolution profile, they do not demonstrate clearly the rates of hydrogen production which are shown in Figure 6.5. At pH 7, the results show high rates of hydrogen production at early times arising mainly from the corrosion of zinc (the corrosion of aluminium at pH 7 is very low). The high production rate for hydrogen is dependent on the assumption of unrestricted water availability at the corroding surface. The rate of hydrogen production drops rapidly once the zinc metal is exhausted but rises again once anaerobic conditions are established. The hydrogen production at this stage results principally from mild steel corrosion and proceeds at this level until the steel is exhausted.

At pH 12, hydrogen production is even higher at early times than for the pH 7 case. This results from the high reactivity of aluminium under alkaline conditions (providing water availability is unrestricted). This hydrogen production rate for aluminium corrosion at pH 12 arises from the (uncoupled) corrosion rate data used (Pryor and Keir 1958). An alternative source (Tabrizi *et al.* 1991) gives a value at pH 12 that is lower by about an order of magnitude, suggesting that the calculated hydrogen production rate might be an over-estimate. In contrast to the pH 7 case, the aluminium is exhausted at an early stage. Once anaerobic conditions are established, hydrogen production occurs only from mild steel corrosion. The rate of this corrosion is about an order of magnitude lower than at pH 7 due to passivation of the steel surface at high pH. Consequently the period of corrosion is extended.

6.1.4 Effect of oxygen ingress rate

The effect of oxygen ingress rate was varied so that the presence of a less effective cap could be investigated.

The oxygen ingress rate was increased by a factor of 100 from that used in the base case calculations described above. Under these conditions, for the thin steel (high surface area) assumption at pH 7, the landfill was not predicted to become anaerobic. Indeed the partial pressure of oxygen was predicted to drop only by about one order of magnitude from its value in air (Table 6.4). The predicted hydrogen evolution in this case was the same as that calculated for the low oxygen ingress rate and low surface area case shown in Figure 6.2. In both cases the landfill was predicted to remain aerobic and no hydrogen generation from mild steel corrosion was predicted.

In a further calculation in which the oxygen ingress rate was increased by a factor of just 10 from that used in the base case calculation, the landfill was again predicted to remain aerobic with a steady-state partial pressure of oxygen of around 1.7×10^{-3} atmospheres.

6.2 Saturated landfill facility

Calculations were performed to investigate whether a landfill with a given waste composition is likely to become anaerobic if it is saturated with leachate. The calculations are relevant to a landfill where water ingress can occur readily filling the waste voidage or to a lower layer of a facility that is saturated after less water has entered. The input parameters for the calculations are given in Table 6.5.

6.2.1 Results for saturated conditions

The numerical results representing aerobic corrosion of mild steel in a saturated system at pH are given in Figure 6.6. These results show that, for the selected aerobic corrosion rate and area of mild steel, the porewater becomes anaerobic relatively rapidly even at shallow depths. At long times or in layers close to the top layer, a steady state is achieved with the oxygen concentration decreasing rapidly with distance. At shorter times or in lower layers, the concentration of oxygen depends only on the extent of corrosion. Below a depth of 0.4 m, the oxygen concentration is reduced by a factor of one thousand from its initial saturated value within 17 days.

Where the porewater becomes anaerobic, it is expected that at anaerobic corrosion will occur at the same rate as calculated for the unsaturated case (see Section 6.1). This is due to the assumption for the unsaturated case calculations that sufficient water is available for corrosion to occur. Similarly, the rates and timescales of aluminium and zinc corrosion are expected to be the same as for the unsaturated case. The hydrogen evolution profiles are therefore expected to be similar to those for the equivalent unsaturated case calculation except that the onset of anaerobic conditions and the hydrogen evolution due to anaerobic mild steel corrosion will occur at a different time and will vary with depth in the upper layers.

6.3 Discussion

The key parameters in determining whether a landfill facility will become anaerobic (in the assumed absence of significant microbial activity) are the relative rates of oxygen ingress and oxygen consumption due to aerobic corrosion of iron and steel.

For the assumed pH conditions and waste composition, it is predicted that the landfill will become anaerobic providing:

- the surface area of the corroding steel is sufficiently high (e.g. thin sheets or particles and lack of protective coatings);
- corrosion is not limited by restricted water availability.

Where these conditions are not met, it is likely that the landfill will remain aerobic.

These results are strongly dependent on the selected aerobic corrosion rates for steel. Reported measurements cover a range of wide values. A further factor that will influence whether anaerobic conditions are established is the hindrance of oxygen ingress due to hydrogen evolution and egress under conditions where the corrosion of zinc and aluminium is rapid.

At early times in a landfill facility, hydrogen production is likely to be high due to zinc corrosion (at pH 7) or aluminium and zinc corrosion (at pH 12), providing water is readily available. Beyond this period, hydrogen production is expected to fall to very low levels if the landfill remains aerobic. If anaerobic conditions are established, hydrogen production is expected to continue due to mild steel corrosion. The rate of hydrogen production by this mechanism decreases significantly at high pH values.

In all the calculations described above, it has been assumed the various metals are uncoupled (i.e. not in physical contact with each other and with water). Where coupling, occurs the rate of corrosion of the more reactive metal can increase dramatically, for example for zinc (ASM 1987) and aluminium (Pryor and Keir 1958) in contact with steel.

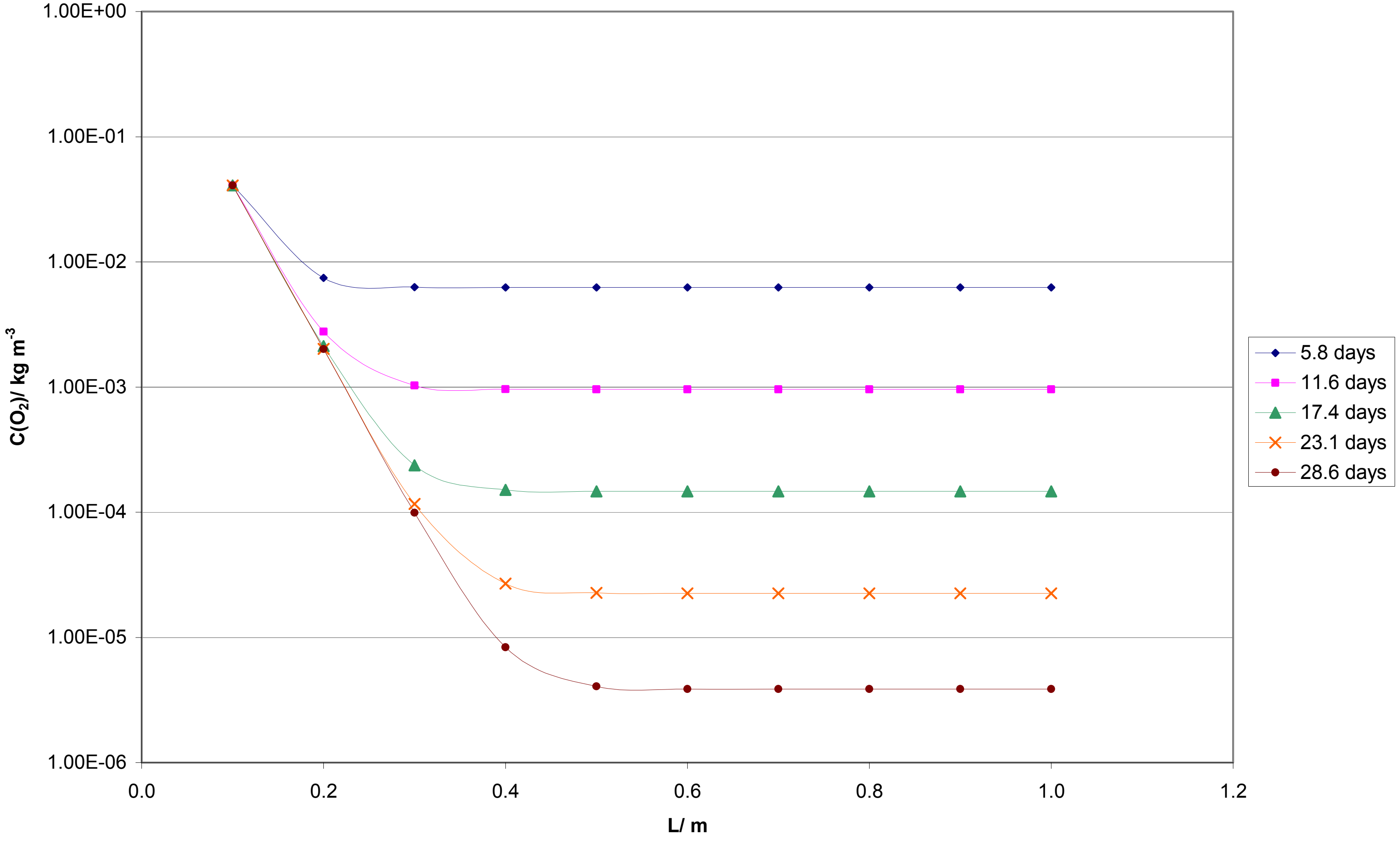
The total volume of hydrogen that might be generated based on the full corrosion of the complete inventory of the mild steel, zinc and aluminium is around 66 times greater than the voidage space in the assumed landfill facility. For the given parameters and assumptions, sufficient hydrogen to fill the voidage is predicted to be generated in 11 days at pH 7, due principally to the corrosion of zinc. At pH 12, this is expected to occur within 2–3 days, due mostly to corrosion of aluminium. Thus at early times the facility could become anaerobic due to displacement of oxygen by hydrogen generated from reactive metal corrosion. Once the zinc (and aluminium at pH 12) are exhausted, aerobic conditions might be re-established if the generation of hydrogen due to anaerobic corrosion of mild steel and/or the consumption of oxygen due to aerobic corrosion of mild steel is too low to maintain anaerobic conditions.

The results described above consider a single waste composition and landfill design. In practice, the results will be strongly dependent on the amounts of corroding metals in the waste and their form. In addition, an actual landfill facility will not be homogeneous. Varying chemical conditions and metal loadings in different regions may affect the evolution of local conditions. In any locally acidic regions, hydrogen production rates due to metal corrosion might be higher than those described above.

The calculations reported have been carried out for a large landfill facility. For a smaller facility, the establishment of reducing conditions is expected to be less likely because the rate of oxygen consumption by corrosion is proportional to the volume of the waste, whereas the rate of oxygen ingress is proportional to the surface area of the cap. The slow filling of a cell will allow greater access of air to the waste so may also decrease the chances that anaerobic conditions are established

The calculations described above were based on available data and limited model development. Further developments that may potentially be useful include:

- development of the model for oxygen ingress to allow for a pressure gradient across the cap and the effect of hydrogen egress (the current study uses a simple approach for oxygen ingress based on an emission of methane for a ‘good cap’ and an assumption that the rate of oxygen ingress/egress is dependent on a diffusion mechanism);
- model development and data assessment for the likely water availability as a function of time;
- more detailed review of the range of aqueous chemical conditions likely to exist in the early anaerobic unsaturated phase and of the corresponding corrosion rates (particularly for mild steel);
- review of the typical unprotected surface area of mild steel likely to be present for a given facility.



See Appendix D for assumptions and boundary conditions and Table 6.3 for input parameters.

Figure 6.6 Predicted variation of oxygen concentration with depth and time in a saturated landfill at pH 7 with an aerobic Top layer and corrosion occurring in all lower layers

7 Possible identification and monitoring methods

7.1 Introduction

The components of landfill gas may be monitored:

- in the field using portable equipment;
- in a sample taken back to a laboratory using more sophisticated equipment.

In general, the portable methods are less costly but are inadequate for quantifying small amounts of a substance or resolving complex mixtures. Since the gas from future landfills containing a high proportion of inorganic material is less likely to be dominated by a few bulk gases, laboratory-based methods of analysis will be more important than has been the case for gas from MSW landfills.

A detailed review of analytical techniques in general is given in the 15 volumes of the *Encyclopedia of Analytical Chemistry* (Meyer 2000). In particular, Volume 3 considers environmental trace gas analysis, while Volumes 4 and 5 include a discussion of field portable instrumentation. These volumes provide a useful background to the range of techniques available.

7.1.1 Portable equipment

Field measurements may be appropriate for the screening of some gases. One of the simplest methods of detecting gaseous species is to use gas detector tubes. These utilise chemical reactions to indicate the presence of gaseous species by observing the resulting colour change in the tube packing. A sample of gas is drawn though the tube by means of a hand-held pump and the length along the tube to which the colour change reaches can provide an indication of the concentration. They are thus simple to use on-site and offer an inexpensive means of analysis. However, they are prone to interferences and are only suitable to indicate the potential presence of the species of interest in landfill gas (Environment Agency 2004a). Appendix E gives a list of species of possible interest in this report that may be detected using tubes from one commercial source (Matheson Tri-Gas), including the measurement ranges and potential interferences. More sophisticated techniques are likely to be required to determine volatile species in gas from future landfills.

Hand-held gas monitoring devices are commonly used for routine measurements at MSW landfills. These instruments generally use:

- infra-red (IR) sensors to measure methane and carbon dioxide;
- an electrochemical sensor to measure oxygen.

They also use selective filters to give an estimate of carbon monoxide and hydrogen cyanide and a number of other constituents that may be present in the gas at the percent level by volume.

Instruments such as those currently supplied by Geotechnical Instruments (UK) Ltd (http://www.geotech.co.uk) and Gas Data Ltd (http://www.gasdata.co.uk) for monitoring bulk gases may be useful to measure methane, carbon dioxide and oxygen in gases from inorganic landfills. The Triple Plus+ monitor from Crowcon (http://www.crowcon.com), for example, can monitor up to four gases including:

- methane (0–100 per cent volume);
- hydrogen sulphide (0–50 ppm);
- carbon monoxide (0–500 ppm);
- nitrogen dioxide (0–10 ppm);
- phosphine (0–5 ppm;)
- ammonia (0–50 ppm;)
- hydrogen (0–2000 ppm ; non flammable levels) ;
- hydrogen cyanide (0–10 and 0–25 ppm).

Although these detection limits may be high compared with the expected concentrations for some species (e.g. phosphine), they are sufficient for others such as hydrogen. Sensors for detecting other species are also available (e.g. from Crowcon).

A portable time-of-flight mass spectrometer has been used to detect a range of volatile organic compounds in landfill gas (Kore Technology 2005). This uses a double membrane inlet system so that no sample preparation is needed. It can be used to quantify mixtures where individual organic compounds (e.g. hydrocarbons and chlorocarbons) are present in the mid ppb to low ppm range.

Allowance should be made for the potentially high flammability of the gases emitted from predominantly inorganic wastes. Although the flux of gas will be lower than from existing MSW waste, the higher proportion of hydrogen may result in a greater probability of gas concentrations being within the flammability range. Hence, it is important to use instruments with an appropriate ATEX rating when working in potentially explosive atmospheres (CEC 1994).

7.1.2 Sampling

Where gas has to be taken to a laboratory for instrumental analysis, methods of representative sampling are required. Several types of gas-tight, inert containers are already used in monitoring existing landfill gas such as:

- stainless steel containers (Schweigkofler and Niessner 1999);
- Tedlar bags (Environment Agency 2003b).

In general, similar methods may be adapted to sampling from inorganic landfills, though Tedlar bags may not be totally inert with respect to some substances. The capture and concentration of minor species on sorption columns (e.g. automated thermal desorption tubes) may be necessary for some species present in gas from inorganic wastes.

7.2 Instrumental methods of analysis

Coupled (or hyphenated) analytical techniques [e.g. gas chromatography–mass spectrometry (GC-MS)] involve the linking of a chromatographic front-end separation technique to a sensitive element-specific detector – typically atomic absorption spectroscopy, atomic emission spectroscopy or mass spectrometry (MS) – for measurement.

‘Non-hyphenated’ techniques (e.g. mass spectrometry) cannot generally achieve such low limits for organometallic analysis, but are useful for screening and are significantly cheaper to purchase and operate. The following is a brief review of the most common ‘hyphenated’ and ‘non-hyphenated’ instrumental techniques available for volatile elemental analysis.

7.2.1 Flame absorption spectroscopy (flame AAS)

Atomic absorption spectroscopy is now rarely used for landfill gas monitoring applications because of its low sensitivity compared with other methods. The technique is therefore limited to screening analysis for mercury after its pre-concentration using the cold vapour technique. Cold vapour (CV) involves the use of a gold or an iodated active charcoal trap to pre-concentrate mercury prior to measurement by flame AAS (CV-AAS) or atomic fluorescence spectroscopy (CV-AFS).

In atomic absorption spectroscopy, the element in its atomic form is introduced into a light beam of appropriate wavelength causing the atom to absorb light (atomic absorption) and enter an excited state. The reduction in intensity of the light beam can be measured and correlated directly with the concentration of the elemental atomic species. This is carried out by comparing the light absorbance of the unknown sample with the light absorbance of known calibration standards.

A typical atomic absorption spectrometer consists of an appropriate light source (usually a hollow cathode lamp containing the element to be measured), an absorption path (usually a flame but occasionally an absorption cell), a monochromator (to isolate the light of appropriate wavelength) and a detector.

The most common form of AAS is called flame atomic absorption. In this technique, a solution of the element of interest is drawn through a flame in order to generate the element in its atomic form. At the same time, light from a hollow cathode lamp is passed through the flame and atomic absorption occurs.

Advantages of AAS

- The technology is relatively inexpensive and the equipment is easy to use.
- Sample throughput is high as each measurement can take only seconds (when the instrument is calibrated).
- The technique is applicable over a wide range of concentrations for most elements.

Limitations of AAS

- AAS is a sequential (only one element at a time) analytical technique. It is better suited to the measurement of small suites of elements as larger suites become progressively uneconomic.
- Interferences from other elements or chemical species can reduce atomisation and depress absorbance, thereby reducing sensitivity.
- Sensitivity is poor in comparison to inductively coupled plasma-mass spectrometry (ICP-MS) and atomic fluorescence spectroscopy (AFS).

7.2.2 Inductively coupled plasma emission spectroscopy (ICP-AES)

Like AAS, poor sensitivity means that ICP-AES is limited in application for landfill gas analysis, but it is used for screening in association with:

- cold vapour (CV-ICP-AES for mercury determination;
- hydride generation (HG-ICP-AES) for arsenic, mercury, antimony and selenium analysis.

In plasma emission spectroscopy, a sample solution is introduced into the core of an inductively coupled argon plasma at a temperature of approximately 8,000°C. At this temperature, all elements become thermally excited and emit light at their characteristic wavelengths. This light is collected by the spectrometer and passes through a diffraction grating that serves to resolve the light into a spectrum of its constituent wavelengths. Within the spectrometer, this diffracted light is then collected by wavelength and amplified to yield an intensity measurement that can be converted to an elemental concentration by comparison with calibration standards. This measurement process is a form of AES.

Advantages of ICP-AES

- Up to 70 elements can be determined simultaneously in a single sample analysis.
- It offers a useful working range over several orders of magnitude.

Limitations of ICP-AES

- The emission spectra are complex and inter-element interferences are possible if the wavelength of the element of interest is very close to that of another element.
- Sensitivity is similar to that of flame AAS with a sensitivity typically 10–100 times less than ICP-MS.

7.2.3 Atomic fluorescence spectroscopy (AFS)

AFS involves measurement of the optical emission from gas-phase atoms that have been excited to higher energy levels by absorption of electromagnetic radiation. Mercury, arsenic, selenium, and antimony can be measured by AFS to significantly lower levels than those achieved by AAS or ICP-AES. Specific methods for use of this technique for mercury speciation are discussed in Section 7.5.1.

The benefits of AFS are high sensitivity and low detection limits for the elements listed above. Speciation of organometallic compounds is achievable by the use of gas chromatography separation prior to CV-AFS detection for mercury or HG-AFS for As, Se and Sb.

7.2.4 Inductively coupled plasma-mass spectroscopy (ICP-MS)

In plasma mass spectroscopy, an inductively coupled argon plasma is used as an excitation source for the elements of interest. But in contrast to ICP-AES, the plasma in

ICP-MS is used to generate ions that are then introduced to a mass spectrometer. These ions are separated and collected by the MS according to their mass-to-charge ratios (*m/e*). The constituents of an unknown sample can then be identified and measured. Different types of ICP-MS are available; their advantages and disadvantages are briefly described below.

Quadrupole ICP-MS (Q-ICP-MS)

This is the most common, and cheapest, ICP-MS. It uses a 'quadrupole' comprising of four cylindrical rods through which are applied radio frequency (RF) and direct current (DC) electric fields. The ions created by the plasma enter the quadrupole and, by tuning the fields of the rods, the ions that can pass through the quadrupole can be selected according to their *m/e* ratio.

Advantages of Q-ICP-MS

- Fast analysis – a mass spectrum of usable data can be acquired in just a few seconds depending on exact instrument settings.
- High sensitivity – modern quadrupoles are able to detect trace levels of many elements at levels well below one ppb (ng g^{-1}).
- A large linear working range of several orders of magnitude.
- Robust, well established technology.

Disadvantages of Q-ICP-MS

- Inability to resolve target isotope easily from molecular interferences – commercially available Q-ICP-MS systems are able to resolve a mass spectrum only to unit resolution. This means that while the mass analyser can easily tell the difference between ^{56}Fe and ^{57}Fe, it cannot resolve ^{56}Fe (mass 55.935) from the ^{40}Ar ^{16}O molecular species (mass 55.957), which is very easily formed in an argon plasma.
- High background noise – the ion optics of quadrupole mass analysers make them susceptible to background noise on the detector, particularly when coupled to an ICP source. High-energy photons from the plasma source can reach the detector sending false pulses into the counting electronics. This increases background noise and results in increased limits of detection (LODs).

High-resolution ICP-MS (HR-ICP-MS)

A typical commercially available high-resolution ICP-MS is able to resolve most isotopes from any molecular species that would otherwise interfere with their analysis. High-resolution systems use a powerful electromagnet with a varying magnetic field rather than an RF/DC field used in a quadrupole.

Advantages of HR-ICP-MS

- Very high sensitivity – high-resolution systems have extremely high ion transport efficiency. This efficiency gives rise to very high levels of sensitivity.
- Low noise – due to the design of the high-resolution mass analyser, there is virtually no chance of any stray photon making its way all the way through the instrument. This results in extremely low background noise, typically

less than 0.2 counts per second. Low noise levels, coupled with very high sensitivity, enable HR-ICP-MS to achieve very low LODs.

Disadvantages of HR-ICP-MS

- Slow analysis speed – the high-resolution mass analyser uses an electromagnet to separate the masses by changing the magnetic field strength between one mass and the next. This takes significantly longer than changing an electrical field.
- Mass drift – at higher resolutions, peaks are extremely narrow, so it becomes much more difficult for the magnet to move to exactly the same mass each time an element is measured. For this reason, high-resolution peaks are always measured by scanning across the entire peak. While this ensures that no counts are missed, peak scanning takes longer than the ‘peak hopping’ used in a quadrupole instrument.
- Price – HR-ICP-MS instruments are expensive and thus may not be commercially viable for landfill gas monitoring purposes.

Time-of-flight ICP-MS (TOF-ICP-MS)

Commercial TOF-ICP-MSs have only been available since 1998, so their use has been so far more limited than quadrupole mass spectrometers. With quadrupole-MS and HR-ICP-MS, the ions of interest are specifically focused to reach the detector but, with TOF, all ions are measured. The ions are accelerated to attain the same kinetic energy, and then pass through a vacuum tube en-route to the detector. The velocity at which the ions pass down the tube is proportional to their *m/e* ratio, with lighter ions reaching the detector before heavy ions. Spectra of the ion population are then captured rapidly and plotted as ion signal versus time calibrated to mass. Thousands of mass spectra per second may be captured, making TOF a very rapid multi-element analyser.

Advantages of TOF-ICP-MS

- Rapid analysis – a mass spectrum of usable data can be acquired in just a few seconds depending on exact instrument settings.
- High sensitivity – similar to that achieved by Q-ICP-MS.
- Simultaneous analysis – multi-element analysis performed simultaneously, with increased resolution from interferences compared with Q-ICP-MS.

Disadvantages of TOF-ICP-MS

- Limited commercial availability.
- High price (though significantly cheaper than HR-ICP-MS).

7.2.5 Hyphenated methods: GC-ICP-MS, GC-CV-AFS, GC-TOF-ICP-MS

The detection systems described above can be linked to a chromatographic front end for trace analysis of organometallic compounds. Gas chromatography (GC) and, to a lesser extent, high performance liquid chromatography (HPLC), are the main separation techniques used.

GC involves a gaseous sample being passed through a chromatographic column that separates the compounds according to their boiling points. The result is that the lighter lower boiling compounds emerge from the column before the heavier compounds. The separated compounds then pass onwards to the elemental analyser for metals analysis.

The benefits of GC separation include

- identification of compounds by comparison of their retention time (time to pass through the column) to standards;
- quantification and speciation of organometallic compounds to trace levels.

GC-ICP-MS is one of the most powerful tools for analysis of volatile elemental species.

Examples of the techniques that have been applied to landfill gas, sewage gas or similar situations to obtain information on trace species of interest are described below.

7.3 Monitoring of gases from existing UK landfills

Gas chromatography is used to analyse gas samples for simple hydrocarbons such as methane, ethane, ethene, etc. as well as for carbon dioxide and hydrogen. The same method can also detect acetylene. Although the proportions of these may be different in gas from inorganic landfilled material, the methodology is still applicable.

Methods for monitoring key trace components of landfill gas from existing MSW landfills are discussed in a series of Environment Agency reports (Environment Agency 2002a, 2003b, 2004b). *Guidance for Monitoring Trace Components in Landfill* ((Environment Agency 2004b) presents current best practice and discusses:

- general monitoring issues;
- recommended approach to monitoring for trace priority components;
- on-site preliminary field measurements;
- protocols for monitoring specific trace components;

It also gives example report formats and recommended detection limits.

Table 7.1 lists the priority trace components to be monitored in gas from existing landfills and recommended detection limits. This list was derived from existing average concentrations found in UK landfill gas and forms the basis of the guidance given in Environment Agency (2004b). This cautions that trace components not identified in Table 7.1 should not initially be disregarded in a site-specific assessment.

Table 7.2 gives examples of substances that would require alternative monitoring techniques.

Table 7.3 summarises the recommended monitoring methods for the classes of components identified:

- hydrogen sulphide;
- speciated VOCs;
- aldehydes;
- total inorganic arsenic;
- total mercury;
- polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs);

- carbon monoxide.

These methods are applicable to monitoring these gases from future landfills containing predominantly inorganic wastes. *Quantification of Trace Components in Landfill Gas* (Environment Agency 2003b) gives more information on sampling techniques and analyses for these gases.

Environment Agency (2002a) makes the following general points concerning these analyses.

- Landfill gas sampling must be carried out with intrinsically safe sampling equipment. This can be achieved with suitable battery-powered equipment. This allows sampling from points where there is insufficient pressure to force gas through sampling devices.
- In most cases, it is preferable to collect sample directly onto the extraction media of choice. Use of a Tedlar bag grab sample and sub-samples taken from this should be treated with caution because the stability of a number of target analytes within a Tedlar bag has not been thoroughly tested.
- The majority of the target VOCs (including the organohalogens and organosulphur compounds) can be determined by collection onto a mixed-bed thermal desorption tube followed by analysis using GC-MS. This technique will also detect many VOCs of lower priority.
- A separate technique must be used for determining methanal (formaldehyde). There is an established and rugged technique for methanal determination involving in-situ derivatisation, which will also detect other carbonyl compounds.
- Hydrogen sulphide can be analysed adequately using real-time hand-held analysers, although the possibility of interferences must be considered.
- The determination of total gaseous mercury using AAS or ICP is recommended as an initial step in a landfill gas survey because both these methods are straightforward. If significant amounts of mercury are measured, then the method described by Lindberg *et al.* (2001) allows the speciation of mercury to be determined.
- The determination of total arsenic by CV-AAS/ICP is recommended before pursuing more complicated techniques that will provide speciation results.

Table 7.1 Priority trace components to be monitored in gas from existing mixed landfills[1]

Significant trace component	Potential impact	Category	Recommended detection limit ($\mu g\ m^{-3}$)
1,1-dichlorethane	Health	Halocarbon	60
1,1-dichlorethene	Health	Halocarbon	90
1,2-dichlorethene	Health	Halocarbon	70
1,3-butadiene	Health	Aliphatic hydrocarbon	70
1-butanethiol	Odour	Organosulphur	300
1-pentene	Odour	Aliphatic hydrocarbon	160
1-propanethiol	Odour	Organosulphur	200
2-butoxy ethanol	Health	Alcohol	200
Arsenic (as As)	Health	Inorganic	0.04
Benzene	Health	Aromatic hydrocarbon	30
Butyric acid	Odour	Carboxylic acid	400
Carbon disulphide	Odour and health	Organosulphur	100
Chloroethane	Health	Halocarbon	120
Chloroethene (vinyl chloride)	Health	Halocarbon	300
Dimethyl disulphide	Odour	Organosulphur	100
Dimethyl sulphide	Odour	Organosulphur	110
Ethanal (acetaldehyde)	Odour	Aldehyde	12
Ethanethiol	Odour	Organosulphur	300
Ethyl butyrate	Odour	Ester	90
Furan (1,4-epoxy-1,3-butadiene)	Health	Ether	70
Hydrogen sulphide	Health and odour	Inorganic	150
Methanal (formaldehyde)	Health	Aldehyde	12
Methanethiol	Odour	Organosulphur	1,000
Tetrachloromethane	Health	Halocarbon	70
Trichloroethene	Health	Halocarbon	40

Notes: [1] Environment Agency (2004b)

Table 7.2 Additional components that may be monitored in gas from existing mixed landfills[1]

Trace component	Potential impact	Category	Recommended detection limit
Mercury (as Hg)	Health	Inorganic	0.5 $\mu g\ m^{-3}$
PCDDs and PCDFs	Health	Chlorinated aromatic	0.1 ng m^{-3} I-TEQ 2)
Carbon monoxide	Health	Inorganic	1 ppmv

Notes: [1] Environment Agency (2004b)
[2] International Toxic Equivalent

Table 7.3 Recommended monitoring methods for trace components in gas from existing mixed landfills[1]

Determinand	Sampling method	Status/standard[2]	Analytical method
Hydrogen sulphide	Direct on-site measurement Gresham tube or Tedlar bag		Gold film portable analyser in real time In the laboratory. After dilution into range of gold film instrument or by GC-MS with no dilution
Speciated VOCs	Dual solid sorbent (ATD tube)	Based on ISO 16017-1	GC-MS using suitable capillary column
Aldehydes	Reactive sorbent (DNPH[3] impregnated silica)	USEPA TO-11	HPLC with UV detection
Total inorganic arsenic	Solid sorbent (activated charcoal/ cellulose filter)	NIOSH 6001	CV-AAS/ICP-MS
Total mercury	Solid sorbent (iodinated charcoal)	NIOSH 6009	CV-AAS/ICP-MS
PCDDs and PCDFs	Solid sorbent (XAD resin column)	NIOSH 5515 Issue 2	HR GC-MS
Carbon monoxide	Gresham tube/Tedlar bag	BS EN 60567:1993	Laboratory GC

Notes:

[1] Environment Agency (2004b)

[2] USEPA = US Environmental Protection Agency; NOISH = National Institute for Occupational Safety and Health (USA)

[3] Dinitrophenylhydrazine

7.4 Elemental analyses of volatile species

Concentrations of elements in volatile species may be determined by ICP-MS or ICP-AAS. It is necessary to sample the gas in the field and transport it to the laboratory for subsequent analysis.

Tedlar bags have been shown to be suitable for sampling volatile metal(loid) compounds species provided analysis can be carried out within a day of sampling (Haas and Feldman 2000). Cryotrapping can be used subsequently to concentrate species prior to analysis (Feldmann and Cullen 1997, Feldmann *et al.* 2001); it also provides a means of longer-term storage in the laboratory. Cryotrapping in the field at a landfill site is likely to be more difficult than sampling into a Tedlar bag (Haas and Feldman 2000), though it would offer longer-term sample stability. Cryotrapping has been used to collect samples of ambient air at –175°C (Pécheyran *et al.* 1998).

In mass spectrometry, the introduction of the sample via a plasma torch (ICP-MS) increases sensitivity but destroys speciation information compared with direct sample introduction after GC (or HPLC) separation. However, coupled with such a separation technique, it can indirectly yield speciation information from the retention behaviour of the unknown on the chromatography column against a known standard. For an element that has a number of isotopes, the isotopic pattern can be used to confirm its identity (Feldmann *et al.* 1998). Pre-concentration by cryotrapping/cryofocusing of volatile species offers useful increases in detection limits (see Section 7.5.3).

The ion population in a plasma depends on its temperature; the higher the temperature the greater the ion population, especially for elements with a high first ionisation potential (McCurdy and Potter 2001). This is illustrated for some elements of interest in Table 7.4.

In mass spectrometry, the possibility of interferences from polyatomic ions formed in the plasma must also be considered; some potential interferences from chlorine and sulphur, both possible common elements in mixed gas samples (e.g. from H_2S and organosulphur species, chlorinated solvents) are shown in Table 7.5.

Other studies on transition metal carbonyls have found it is almost impossible to detect ^{52}Cr and ^{53}Cr in landfill gas because of interference from $^{40}Ar^{12}C^+$ and $^{40}Ar^{13}C^+$ (Feldmann and Cullen 1997). Iron and manganese detection is hindered by $^{40}Ar^{14}N^+$ ($^{54}Fe^+$), $^{40}Ar^{14}N^1H^+$ ($^{55}Mn^+$), $^{40}Ar^{16}O^+$ ($^{56}Fe^+$) and $^{40}Ar^{16}O^1H^+$ ($^{57}Fe^+$). Similarly, nickel and cobalt determination may suffer from interferences from the doubly-charged ions formed from volatile tin compounds, e.g. $^{116}Sn^{2+}$ ($^{58}Ni^+$), $^{118}Sn^{2+}$ ($^{59}Ni^+$), $^{120}Sn^{2+}$ ($^{60}Co^+$, $^{60}Ni^+$) and $^{124}Sn^{2+}$ ($^{62}Ni^+$) (Feldmann and Cullen 1997).

Table 7.4 Calculated ion population (%) as a function of plasma temperature for some elements of interest[1]

Element	Ionisation potential (eV)	Plasma temperature			
		5,000K	6,000K	7,000K	8,000K
Pb	7.42	4.3	51.2	91.1	98.3
Sb	8.64	0.3	9.0	57.6	90.9
Cd	8.99	0.1	4.8	43.2	85.7
Se	9.75	0.0	1.1	17.8	66.6
As	9.81	0.0	1.0	16.4	64.6
Hg	10.43	0.0	0.3	6.5	42.6

Notes: [1] From McCurdy and Potter (2001)

Table 7.5 Some potential isotopic interferences in ICP-MS[1]

Element	Isotope	Potential interference
Titanium	47	$^{35}Cl^{12}C$
Vanadium	51	$^{35}Cl^{16}O$
Chromium	52/53	$^{35}Cl^{16}O^1H$ / $^{37}Cl^{16}O$
Manganese	55	$^{37}Cl^{18}O$
Iron	57	$^{40}Ar^{16}O^1H$
Cobalt	59	$^{23}Na^{35}Cl^1H$
Nickel	60	$^{23}Na^{37}Cl$
Copper	65	$^{32}S^{32}S^1H$, $^{32}S^{16}O^{16}O^1H$
Zinc	66	$^{32}S^{34}S$, $^{35}Cl^{16}O^{14}N^1H$
Arsenic	75	$^{40}Ar^{35}Cl$
Selenium	82	$^{34}S^{16}O^{16}O^{16}O$

Notes: [1] McCurdy and Potter (2001)

Bouyssiere *et al.* (2001) reported that GC-ICP-MS is a factor of 100–1,000 more sensitive than GC-MIP-AES and GC-MS for arsenic in natural gas condensates. They cite detection limits of approximately 5 pg for trimethylarsine in natural gas and 0.5 ng for a range of methylated/alkylated arsines by GC-MS from other studies compared with 0.05 pg arsenic by GC-ICP-MS.

A list of absolute detection limits for some elements with volatile compounds using GC-ICP-MS is given in the third column of Table 7.6. Feldmann et al. (1998) successfully used cryotrapping and GC fractionation to obtain fractions containing species of interest in the ng cm^{-3} concentration range and identified trimethylstibine and tetramethyltin in landfill gas, and trimethylbismuth in sewage gas, directly using MS.

Hetland *et al.* (1991) trapped $Ni(CO)_4$ and $Fe(CO)_5$ on activated carbon and quote typical detection limits of 0.0004–0.00008 mg m^{-3} and 0.15–0.006 mg m^{-3} respectively, based on sampling volumes of 100 dm^3 and detection by AAS/AES.

A review of methods for the determination of tin in environmental samples concentrated on analysis of solid and water samples (Leroy *et al.* 1998). From this review it is apparent that sample work-up by derivatisation to hydride or alkylated species followed by gas chromatography and detection by AAS or flame photometric detection is commonly employed and that cryogenic pre-concentration may be used to improve sensitivity. Such concentration, separation and detection techniques would be applicable to the collection and analysis of volatile tin species released from landfill.

Table 7.6 Detection limits for volatile elements using GC-ICP-MS[1]

Element	m/z	Absolute LOD[2] (pg)	LOD for 20 dm^3 gas sample[3] ($pg\ m^{-3}$)
Germanium	73	0.03	1.6
Arsenic	75	0.54	26
Selenium	77	0.42	21
Selenium	82	0.66	33
Cadmium	113	0.27	14
Tin	120	0.29	15
Antimony	121	0.15	7.6
Tellurium	126	0.13	6.7
Iodine	127	0.21	10
Mercury	202	0.78	39
Lead	208	0.86	43
Bismuth	209	0.09	4.7

Notes:
[1] Feldmann (1997)
[2] Calculated based on three times the standard deviation of the blank signal.
[3] Cryotrapped sample

7.5 Speciation analyses

7.5.1 Mercury speciation

A method for analysing total mercury was identified in Section 7.3. An alternative approach (Lindberg *et al.* 2001) uses a sampling technique that allows the speciation of mercury compounds – for a summary, see Environment Agency (2002a).

Total gaseous mercury can be collected on gold or iodated active charcoal traps and analysed by CV-AFS after acid digestion of the traps. Landfill gas is generally saturated with water vapour so, to eliminate condensation, the charcoal traps are heated to about 50°C (slightly above the landfill gas temperature) and preceded by cold traps. Dimethyl mercury compounds can be sampled using Carbotrap™ absorbers and cold traps located upstream of separate Carbotraps™ for monomethyl mercury in the landfill gas condensate. Analysis is by thermal desorption (TD) chromatography with atomic fluorescence detection after isolating monomethyl mercury from the matrix by distillation and conversion of methylethyl mercury by aqueous phase ethylation.

This method has been used subsequently to measure total gaseous mercury, dimethyl mercury and monomethyl mercury (Lindberg *et al.* 2005). Total airborne mercury (organic and inorganic) was trapped using iodated activated charcoal traps in tandem. These traps were then leached with a mixture of hot nitric and sulphuric acids, oxidised with BrCl solution and the total recovered mercury measured with CV-AFS. Dimethyl mercury was collected on a light-shielded Carbotrap™ and analysed by TD-GC-AFS. The output of the GC was passed through a pyrolytic cracking column at 700°C to convert organic mercury to elemental mercury prior to entering the CV-AF spectrometer. Dimethyl mercury was identified by retention time. Trapping of monomethyl mercury made use of the fact that, in air, it is probably present as a halide or hydroxide, and is stable and soluble in dilute hydrochloric acid. Monomethyl mercury was trapped in a series of three, light-shielded impingers containing 0.001 mol dm^{-3} hydrochloric acid. Sample work up in the laboratory was by a combination of distillation, ethylation and Carbotrap™ pre-concentration, followed by TD-GC-AFS in a similar manner to the analyses for dimethyl mercury.

An unknown interference with dimethyl mercury collection and analysis is reported (Lindberg *et al.* 2005). This can be minimised by reducing the volume of landfill gas collected and using two Carbosorb traps in series to collect dimethyl mercury. Lindberg *et al.* (2005) concluded that the most accurate dimethyl mercury concentrations would be obtained by collecting the smallest sample volume possible.

Using these methods the following approximate ranges were measured:

- total gaseous mercury concentrations (10^1 to 10^4 ng m^{-3});
- dimethyl mercury concentrations (4 to 80 ng m^{-3});
- monomethyl mercury concentrations (2 to 40 ng m^{-3}).

Lindberg *et al.* (2005) report a method detection limit of ~5 pg m^{-3} for dimethyl mercury, although this depends on sample volume and may be compromised by the interference with trapping discussed above.

The ESART study used an in-series sample train consisting of a moisture trap (aqueous mercury), iso-octane (gaseous organic mercury), Orbo™ activated carbon (gaseous non-elemental mercury) and gold Amasil (gaseous elemental mercury). Analysis was by AFS after appropriate sample treatments (ESART 2003).

7.5.2 Trapping and analysis of phosphine, arsine and stibine

The use of filters impregnated with silver nitrate to collect phosphine (arsine and stibine may also be collected simultaneously) is discussed by Demange *et al.* (2000) in work based on the method proposed by Hetland *et al.* (1991).

Sample work-up is by dissolution of the filters in acid with analysis for phosphorus by ICP-AES and a detection limit of better than 1 µg of phosphorus per filter was achieved. Interferences from species that react with silver nitrate are possible. However, a sampling methodology was developed to prevent reaction with H_2S and NH_3 by using impregnated pre-filters to remove these species (which may also allow their determination). Such pre-filters may also prevent interferences from acids (e.g. HCl) and particulates. Hetland *et al.* (1991) quotes typical detection limits of 0.003 mg m^{-3} (by ICP-AES) and 0.001 mg m^{-3} by electrothermal AAS (ETAAS) for phosphine and 0.001 mg m^{-3} (ICP-AES) and 0.0001 mg m^{-3} (ETAAS) for arsine and stibine, based on a sampled volume of 1 m^3 over 8 hours.

In sampling of landfill gas for phosphine (Roels and Verstraete 2004), phosphine was analysed by GC (with thermal conductivity and thermionic-specific detection) in samples of landfill gas collected in 1 dm^3 glass bottles. The concentrations of phosphine (~ 3–32 µg m^{-3}) were sufficiently high that the LOD was exceeded when a 500 µdm^3 sample loop was used. Therefore, cryogenic trapping was not necessary in this study. However, the method was developed to measure lower phosphine concentrations and a detection limit of 4 ng m^{-3} from cryotrapping 100 cm^3 of gas is reported (Roels *et al.* 2002).

7.5.3 Speciation of carbonyls and alkylated elements

The use of ICP-MS to obtain information on elements present in volatile compounds is discussed in Section 7.4. It may be coupled with a separation technique to provide speciation information (e.g. using the retention time obtained from gas chromatography). Feldmann and Cullen (1997) describe the use of cryogenic trapping followed by cryofocusing to analyse molybdenum and tungsten carbonyls in landfill gas. After collection of gas samples in Tedlar bags (4 dm^3 for landfill gas, 80 dm^3 for ambient air above the landfill), the volatile species were trapped on Chromosorb™ at –78°C (at this temperature condensation of carbon dioxide and methane was avoided). The volatile species were then volatilised from the trap by raising its temperature to 150°C and re-trapped in a second Chromosorb™ trap held at -196°C. The volatile species were then desorbed from the second trap into helium carrier gas by raising the column temperature from –196 to 150°C over a period of 3 minutes. This provided chromatographic separation of the volatile species prior to passage through the torch of the ICP-MS and allowed their potential identification on the basis of retention time or comparison with known standards.

In addition to the measurement of the molybdenum and tungsten hexacarbonyls at concentrations of a few ng m^{-3} to a few hundred ng m^{-3}, it is reported that arsines, trimethylstibine, and tetramethyltin and higher alkylated tin species were found at concentrations of µg m^{-3}. Dimethylselenide, dimethyltellurium, dimethylmercury, elemental mercury, trimethylbismuthine, tetramethyllead and tetraethyllead were found at concentrations of ng m^{-3}. Feldmann and Cullen (1997) do not discuss factors controlling detection limits for the technique explicitly but detectable concentrations of 0.1 ng m^{-3} in ambient air are suggested in the text, implying a collected mass of 8 pg from 80 dm^3. The last column of Table 7.6 gives GC-ICP-MS detection limits for some elements in 20 dm^{-3} of gas after cryotrapping. These range from 1.6 pg m^{-3} for germanium to 43 pg m^{-3} for lead.

A subsequent study by Feldmann (1999) used the same technique to measure nickel tetracarbonyl, iron pentacarbonyl, molybdenum hexacarbonyl and tungsten hexacarbonyl in sewage gas. A detection limit of 0.01 µg m^{-3} for nickel is estimated if 1 dm^3 of gas is sampled (equivalent to 10 pg nickel); this can be increased to 0.001 µg m^{-3} if 10 dm^{-3} is sampled. This compares with cited detection limits of around 70 µg m^{-3} for direct mass spectrometry (Campana and Risby 1980) and IR spectrophotometry (McDowell 1971), techniques capable of direct speciation (Feldmann 1999). The detection limit is similar to a cited possible detection limit of 0.09 ng nickel for on-line pre-concentration of nickel carbonyl (Erber and Cammann 1995) followed by graphite furnace-AAS (Filkova and Jäger 1986), although AAS avoids potential ion interference problems that may occur in ICP-MS (Feldmann 1999).

Analysis of stibine, monomethylstibine, dimethylstibine and trimethylstibine in microbial laboratory experiments by solid phase microextraction followed by GC-MS with cryogenic focusing has been described (Smith *et al.* 2002). Trimethylstibine has also been determined in microbial laboratory experiments by:

- GC-MS and GC-AAS (Jenkins *et al.* 1998);
- capillary GC with fluorine-induced chemiluminescence and GC-MS (Gürleyük *et al.* 1997);
- cryotrapping coupled with GC-ICP-MS (Andrewes *et al.* 1999).

Trimethylarsine was also found in the latter study.

7.5.4 Reduced sulphur species

Gas chromatography has been used to determine reduced sulphur species in landfill gas (Kim *et al.* 2005). Sample detection limits (as sulphur) using pulsed flame photometric detection are reported as 17 pg (hydrogen sulphide), 7 pg (methyl mercaptan), 4 pg (dimethylsulphide), 3 pg (carbon disulphide) and 5 pg (dimethyl disulphide). With a direct injection and a sample loop volume of 500 µdm^3, this gives detection limits for sulphur of 6 (CS_2) to 34 (H_2S) µg m^{-3} in the gas as collected. Lower detection limits may be achieved by cryofocusing prior to gas chromatography.

7.5.5 Hydrogen cyanide

Reported methods for the detection of hydrogen cyanide in air generally involve pumping air samples through a solid or liquid able to trap and/or react with HCN (Juillet *et al.* 2005). Reaction products may then be analysed by a range of techniques including ion chromatography, spectrophotometry and potentiometry.

Some of these methods may be complex, not specific for cyanide and suffer from interferences. Juillet *et al.* (2005) describe an examination of five different adsorbents (Tenax GR, Carbotrap B, Carboxen 563, Carboxen 569 and Cardosieve S-III) for trapping of hydrogen cyanide prior to analysis by ATD-GC-MS. Their study included the effect of sample humidity on trapping. They concluded that the molecular sieves (Carboxen 563, Carboxen 569 and Cardosieve S-III) displayed sufficiently robust trapping qualities to be of use; Carbosieve S-III was the most suitable of the three. Achievable hydrogen cyanide detection limits down to sub-ppm levels are suggested using 200 mg of this sorbent.

7.5.6 Siloxanes

A number of methods are available for analysing siloxanes in gas samples and no standard method has been adopted (Environment Agency 2004c).

The use of GC coupled with MS and AES to obtain speciation information on silicon species in landfill and sewage gas has been described (Schweigkofler and Niessner 1999). This work also included the analysis of a range of VOCs. Samples were collected in evacuated 15 dm^3 stainless steel containers with electropolished internal surfaces. They were usually analysed within 36 hours of collection. Recovery of lower molecular weight siloxanes (and VOCs) was greater than 90 per cent from a standard gas mixture in nitrogen after 2 hours storage.

However, due to sorption losses within the sample container, recovery of low volatility siloxanes (e.g. decamethylcyclopentasiloxane, b.p. 210°C, 85-90 per cent recovery; dodecamethylpentasiloxane, b.p. 223°C, 35 per cent recovery) were less than 90 per cent and the sample collection method could not be used for quantitative determination of less volatile siloxanes. Loss to the vessel walls increased with increasing boiling point and polarity of the compound. Sample stability was checked by storing a sample of biogas and a sample of standard gas mixture for 10 days prior to analysis. Samples were concentrated by cryotrapping/cryofocusing, then split and injected in parallel to two GC systems with MS or AE detection capabilities. Column lengths were adjusted to take account of the pressure differences between the two detection techniques and allowed simultaneous detection of the analysed species. Seven silicon species were detected in samples of landfill gas from two German domestic waste disposal sites: trimethylsilanol, hexamethyldisiloxane, octamethylcyclotetrasiloxane, decamethylcyclopentasiloxane (concentrations typically in 1 to 10 mg m^{-3} range), hexamethylcyclotrisiloxane, octamethyltrisiloxane and decamethyltetrasiloxane (concentrations typically <0.01 to 0.5 mg m^{-3}) (Schweigkofler and Niessner 1999).

7.6 Conclusions

The following can be concluded from this review of possible methods for monitoring and identifying volatile species in gas from inorganic landfills.

- There are recommended methods for measurement of hydrogen sulphide, total inorganic arsenic, total mercury and carbon monoxide (Environment Agency 2004b).
- Portable monitors offer some possibilities for monitoring species such as hydrogen at levels of interest. However, they may not be sensitive enough to measure the concentration of some other trace species. Laboratory-based methods (e.g. gas chromatography currently used to monitor simple hydrocarbons) can be applied to analysis of species such as hydrogen, carbon dioxide, methane and acetylene, which may be present in gas from inorganic wastes. Methods of collecting samples in Gresham tubes, for instance, are similar to those already employed in gas monitoring boreholes on existing MSW sites.
- Cryogenic trapping and focusing, coupled with GC and ICP-MS or ICP-AAS, appear promising techniques capable of analysing for a range of organic and inorganic trace species (both ICP-MS and ICP-AAS may be required to resolve uncertainties caused by interferences). GC-MS would also be useful although it is less sensitive. Other mass spectrometry techniques may also be applied and offer benefits in some circumstances (e.g. HR-ICP-MS offers high sensitivity and resolution, TOF-ICP-MS offers rapid multi-element analysis) but at increased cost.
- Sensitive mercury analysis may be achieved using atomic fluorescence coupled with appropriate sampling, pre-concentration and sample work-up.
- Monitoring of hydrides by trapping on silver nitrate impregnated filters followed by sample work-up and analysis by ICP-AES or ETAAS would be applicable to phosphine, arsine and stibine. This is likely to be of use for analysis of other hydrides, though the potential interference from acetylene may be a problem.
- Reduced sulphur species may be analysed by GC. Hydrogen cyanide has been measured by ATD-GC-MS. Siloxanes have been determined by GC coupled with MS and AES, although losses of low volatility species in samples stored in stainless steel containers have been reported.
- Analytical methods of sufficient sensitivity exist for all the species likely to be of interest in gas emissions from future landfills containing waste that have higher concentrations of inorganic materials than existing landfills. However, many of the analyses are likely to be laboratory-based rather than ‘in-field’ measurements and will require a number of different methods to be employed to cover the range of compounds likely to be present.

8 Assigning priorities to compounds for monitoring

A range of compounds has been identified in Sections 4 and 5 as possibly being present in gas from future landfills containing a high proportion of inorganic material. Monitoring methods for these compounds are discussed in Section 7.

The need to monitor for a particular compound will depend upon the hazard caused by its presence. For an individual compound, its relative hazard in a gas mixture will depend upon its concentration and properties such as toxicity, flammability and odour. However, few data are available for the concentrations of the typical species that may be present in the gas produced. Thus, in order to suggest priority compounds to be monitored in any initial sampling of gas from inorganic landfills, only simple qualitative screening can be used at this stage.

Table 8.1 compares the concentrations of trace species in landfill gas (or other samples), as given in Table 5.7 with the Long-Term Workplace Exposure Limits (LTWELs) (HSE 2005) or other typical exposure limits. Where data are available, the concentrations of many of the species in gas from existing landfills or in sewage gas are several orders of magnitude below the exposure limits. In these cases, however, dilution by bulk gas may be significant and some species (e.g. alkylated tin compounds, volatile arsenic) have been found at concentrations comparable with exposure limits.

A simple qualitative screening of the possible trace components in gas from landfills containing a high proportion of inorganic wastes has been made in order to suggest priority compounds for initial monitoring. It is assumed that the bulk gas components monitored routinely for existing landfills (methane, carbon dioxide and oxygen) (Environment Agency 2004a) would continue to be monitored. These gases provide an indication of the chemical and microbial conditions within a landfill and thus give some basis on which trace component data for different sites may be compared. It is suggested that hydrogen should also be monitored routinely as a possible contributor to bulk gas production.

Compounds were screened qualitatively against:

- the possibility of being toxic, flammable, malodorous or explosive in air;
- their detection in existing landfill gas;
- their concentration in gas from existing landfills being ≤1 per cent of the Long-Term Workplace Exposure Limit (or no LTWEL set). (Table 8.1 compares the concentrations of trace species in landfill gas – or other samples – as given in Table 5.7, with the LTWELs or other typical exposure limits);
- their formation in the absence of microbial action.

The screening against toxicity, flammability, explosive hazard and odour does not take account of the concentrations that may be required to pose a hazard. This preliminary screening, based on current understanding and very limited sample data, gives the following groups in terms of priority:

- **Highest priority**: amines, AsH_3, COS, CS_2, HCN, H_2S, H_2Se, NH_3, $Ni(CO)_4$, $Pb(CH_3)_4$, $Pb(C_2H_5)_4$, PH_3 and SbH_3

- **Medium priority**: CO, CH_3SH, $(CH_3)_4Sn$ and other alkylated Sn compounds, $(CH_3)_3As$, $(CH_3)_2S_2$, $(CH_3)_2S$, alkylated Pb (other than tetraethyl and tetramethyl), monomethylmercury, $(CH_3)_2Te$, $(CH_3)_3Sb$, $COCl_2$, NO_X, hydrogen halides (HF and HCl), alkylated Ge.
- **Lowest priority**: $(CH_3)_2Se_2$, Hg^0, $Hg(CH_3)_2$, simple hydrocarbons (e.g. acetylene but excluding methane), alkylated arsenic (other than $(CH_3)_3As$), CH_3I, alkylated silicon, CSe_2, metal carbonyls (e.g. $Mo(CO)_6$, $W(CO)_6$ but excluding $Ni(CO)_4$), alkylated antimony (other than $(CH_3)_3Sb$), $(CH_3)_3Bi$, $(CH_3)_2Se$, siloxanes.

When applying these groupings, it will also be necessary to consider the nature of the disposed waste in deciding on the trace compounds that are of highest priority for monitoring (remembering that hydrogen is assumed to be monitored as a possible bulk gas). This is especially the case for monofills or for landfills where only a few waste types are present. For example, although acetylene is classified above as being of a low priority, it would be a high priority for those landfills receiving significant amounts of waste from metal refining processes because of the potential presence of carbides in such wastes.

Some of the species identified as being of highest priority (e.g. hydrogen sulphide, hydrogen cyanide and ammonia) may be detected at ppm levels using portable monitors (e.g. those currently available from Crowcon).

Only one of the compounds identified as being of high priority (hydrogen sulphide) has a recommended method developed for existing landfill gas monitoring, although arsine would have been collected by the methodology for determining total inorganic arsenic (Environment Agency 2003b, 2004b).

Possible methods for the trace monitoring of the remaining compounds or identifying those elements present in a volatile form can be identified from the review in Section 7.

- Arsine, phosphine and stibine may be trapped using filters impregnated with silver nitrate and analysed by ICP-AES (Demange *et al.* 2000) (see Section 7.5.2).
- Hydrogen cyanide can be trapped on molecular sieves and analysed by ATD-GC-MS (Juillet *et al.* 2005) (see Section 7.5.5).
- Cryotrapping allows species to be concentrated and, coupled with appropriate instrumentation, has provided a means of determining (see Sections 7.5.2, 7.5.3 and 7.5.4):
  - phosphine (and potentially arsine and stibine) by GC;
  - tetramethyllead, tetraethyllead and nickel carbonyl by ICP-MS;
  - carbon disulphide, hydrogen sulphide (and potentially carbonyl sulphide and hydrogen selenide) by GC.

Table 8.1 Some typical exposure limits for gaseous trace species likely to be generated in inorganic landfills[1.6]

Species	Toxic?	Typical concentration[2] in gas from existing landfills (or other experiments[3]) (g m^{-3})	Long-term WEL[4] (g m^{-3})	Other information on exposure limits[5]
Group VIa				
$Mo(CO)_6$	Y	1×10^{-8} to 3×10^{-7}	–	Long-term WEL = 5×10^{-3} g m^{-3} (soluble Mo compounds) (HSE 2005)
$W(CO)_6$	Y	5×10^{-9} to 2×10^{-7}	–	Long-term WEL = 1×10^{-3} g m^{-3} (soluble W compounds) (HSE 2005)
Group VIII				
$Ni(CO)_4$	Y	(5×10^{-7} to 1×10^{-6})***	–	Short-term (15 minute) WEL = 2.4×10^{-4} g m^{-3} (HSE 2005)
Group IIb				
Hg^0	Y	9×10^{-7} 1×10^{-8} to 1×10^{-5}	–	Typical TLV/TWA = 5×10^{-5} g m^{-3}, typical PEL = 1×10^{-4} g m^{-3}
$Hg(CH_3)_2$	Y	1×10^{-7} 5×10^{-9} to 8×10^{-8}	–	No data
$(CH_3)HgX$	Y	2×10^{-9} to 4×10^{-8}	–	No data

Table 8.1 (cont'd) Some typical exposure limits for gaseous trace species likely to be generated in inorganic landfills[1.6]

Species	Toxic?	Typical concentration[2] in gas from existing landfills (or other experiments[3]) (g m^{-3})	Long-term WEL[4] (g m^{-3})	Other information on exposure limits[5]
Group IVb				
Simple hydrocarbons excl methane (acetylene used as example)	N		–	No known toxic effects for acetylene
CO	Y	6×10^{-3} (median)	3.5×10^{-2}	–
CO_2			9.15	
$COCl_2$	Y	–	8×10^{-5}	–
HCN	Y	–	–	Short-term WEL = 1.1×10^{-2} mg m^{-3} (HSE 2005)
Silane, SiH_4			6.7×10^{-4}	–
Germane, GeH_4			6.4×10^{-4}	–
$(CH_3)_4Sn$	Y	1×10^{-4}	–	Long-term WEL = 1×10^{-4} mg m^{-3} (organic Sn, as Sn) (HSE 2005)
Other alkylated tin compounds (unknown)	Y?	3×10^{-5}	–	Long-term WEL = 1×10^{-4} mg m^{-3} (organic Sn, as Sn) (HSE 2005)
$Pb(CH_3)_4$	Y	'ng per m^3 range'	–	"Very toxic"
$Pb(CH_3)(C_2H_5)_3$	Y	4×10^{-8}	–	–
$Pb(C_2H_5)_4$	Y	1×10^{-6} 'ng per m^3 range'	–	–

Table 8.1 (cont'd) Some typical exposure limits for gaseous trace species likely to be generated in inorganic landfills[1.6]

Species	Toxic?	Typical concentration[2] in gas from existing landfills (or other experiments[3]) (g m^{-3})	Long-term WEL[4] (g m^{-3})	Other information on exposure limits[5]
Group Vb				
NOx (for NO_2)	Y	–	–	For NO_2 typical PEL = 5 ppm, Long-term OEL = 3 ppm, 6×10^{-3} g m^{-3}
NH_3	Y	–	1.8×10^{-2}	
Amines (for example of trimethylamine	Y	–	–	Triethylamine long-term WEL = 8 mg m^{-3}, Dimethylamine long-term WEL = 3.8 mg m^{-3} (HSE 2005)
PH_3	Y	3×10^{-6} to 3×10^{-7}	–	Short-term WEL = 4.2×10^{-4} g m^{-3} (HSE 2005)
AsH_3	Y	7×10^{-8}	1.6×10^{-4}	-
CH_3AsH_2	Y?	4×10^{-6}	–	No data
$(CH_3)_2AsH$	Y?	1×10^{-8}	–	No data
$(CH_3)_3As$	Y	4×10^{-6}	–	No data
$(CH_3)_2As(C_2H_5)$	Y	4×10^{-8}	–	No data
$As(C_2H_5)_3$	Y	–	–	No data
Total volatile arsenic (unspeciated)	Y?	6×10^{-7} to 4×10^{-4}	–	Long-term WEL for arsenic and its compounds except arsine = 1×10^{-4} g m^{-3}) (HSE 2005)
$(CH_3)_3Sb$	Y?	1×10^{-4} (2×10^{-4})**	–	No data
SbH_3	Y	(2×10^{-4})**	–	No data
$(CH_3)_2SbH$	Y?	(2×10^{-5})**	–	No data
$(CH_3)SbH_2$	Y?	(2×10^{-5})**	–	Long-term WEL for Sb and its compounds except SbH_3 = 5×10^{-4} g m^{-3}(HSE 2005)
$(CH_3)_3Bi$		1×10^{-6} $(4 \times 10^{-5}$ to $1 \times 10^{-4})$**	–	No data

Table 8.1 (cont'd) Some typical exposure limits for gaseous trace species likely to be generated in inorganic landfills[1,6]

Species	Toxic?	Typical concentration[2] in gas from existing landfills (or other experiments[3]) (g m^{-3})	Long-term WEL[4] (g m^{-3})	Other information on exposure limits[5]
Group VIb				
H_2S	Y	3×10^{-2} to 6×10^{-1} *	7×10^{-3}	
CS_2	Y	1×10^{-3} to 2×10^{-1} *	3.2×10^{-2}	
COS	Y	–	–	'Harmful at levels from 100 ppm upwards'
$(CH_3)_2S_2$	Y	$<3 \times 10^{-5}$ to 1×10^{-2} *	–	No data
CH_3SH		33 to 22,550 ppb	1×10^{-3}	(Long-term WEL ≡ 0.5 ppm (HSE 2005))
$(CH_3)_2S$	Y	33 to 7,120 ppb	–	No data
$(CH_3)_2Se$	Y	(6×10^{-5})**	–	No data
H_2Se	Y	–	0.02 ppm as Se	
$(CH_3)_2Se_2$	Y?	2×10^{-8} (3×10^{-4})**	–	'May be fatal if inhaled'
CSe_2	Y	–	–	No data
$(CH_3)_2Te$	Y	1×10^{-7} (3×10^{-6})**	–	No data
Group VIIb				
Hydrogen halides	Y (HF HCl)	–	HF(as F) = 1.5×10^{-3} HCl = 2×10^{-3} HBr = –	Short-term WEL HF = 2.5×10^{-3} g m^{-3} (HSE 2005) Short-term WEL HCl = 8×10^{-3} g m^{-3} (HSE 2005) Short-term WEL HBr = 1×10^{-2} g m^{-3} (HSE 2005)
CH_3I	Y	–	1.2×10^{-2}	-

Notes:

[1] N =No, Y=Yes based on data from various sources, Y? or N? = Yes or No based on judgement by analogy with similar compounds, - = not possible to make a judgement (or, for mixed species, not applicable).

[2] Concentrations as the elements unless otherwise noted by * (* =concentration of molecular species)

[3] (Other experiments) denoted in ( ) are for gas samples taken from above incubated sewage sludge or *M. formicicum* cultures in laboratory experiments** , or gas sampled from sewage treatment plants***

[4] HSE (2005)

[5] Unless referenced otherwise, taken from data on the websites of the School of Chemistry, Bristol University (http://www.chm.bris.ac.uk/safety/Explimits.htm) and the Physical and Theoretical Chemistry Laboratory, Oxford University (http://physchem.ox.ac.uk/MSDS).

[6] WEL = Workplace Exposure Limit (long-term = 8-hour time weighted average (TWA) reference period, short-term = 15-minute reference period) (HSE 2005); PEL = Permissible Exposure Limit defined by (TWA) or absolute value; LTEL = Long-term Exposure Limit; OEL = Occupational Exposure Limit; TLV = Threshold Limit Value.

Table 9.1 Summary of available gas treatment methods and possible application to components of landfill gas

	Combustion			Wet scrubbers					Absorbers	
	Combustion only (flaring)	Thermal (post-combustion)	Catalytic (post-combustion)	Acid scrubber	Alkali scrubber	Oxidising scrubber	Solvent scrubber	Water scrubber	Activated carbon	Zeolites
Hydrogen	Y	Y	Y	N	N	Y	N	N	N	N
Hydrogen sulphide	Y	Y	N	Y[2]	Y	Y	Y	Y	Y	Y
Carbon dioxide	N	N	N	N	N	Y	Y	Y	Y	Y
Carbon monoxide	Y	Y	Y	N	N	Y	N	N	Y	Y
Methane	Y	Y	Y	N	N	Y	N	N	Y	Y
NO_X compounds	N	N	Y	Y[3]	Y	Y	Y	Y	Y	Y
Hydrogen cyanide	N	Y[1]	Y	N	Y	Y	N	N	Y	Y
Hydrogen halides	N	Y[1]	N	N	Y	Y	N	N	Y	Y
Metal carbonyls	N	Y[1]	Y	N	N	Y	N	N	Y	Y
Ammonia	N	Y[1]	N	Y	N	N	N	Y	Y	Y
Amines	N	Y[1]	N	Y	N	N	N	Y	Y	Y
Carbon disulphide	Y	Y[1]	N	Y[2]	Y	Y	N	Y	Y	Y
Phosphine	N	Y[1]	Y	N	N	N	N	N	N	N
Arsine	N	Y[1]	Y	N	N	N	N	N	N	N
Stibine	N	Y[1]	Y	N	N	N	N	N	N	N

Notes:

[1] Dependent on temperature and residence time.

[2] With sulphuric acid scrubber.

[3] With nitric acid scrubber.

9 Potential gas treatment methods

In Section 2.2.2 it was noted that measures should be taken in order to control the accumulation and migration of landfill gas in all forms of landfill site. This section considers the potential methods for treating a gas stream with the following characteristics that may be typical of that produced from a predominantly inorganic landfill:

- main constituent: hydrogen:
- also containing: hydrogen sulphide, carbon dioxide, carbon monoxide, methane and NO_x compounds;
- trace gases include: hydrogen cyanide, hydrogen halides, metal carbonyls, ammonia, amines, carbon disulphide, phosphine, arsine and stibine.

Table 9.1 summarises the various treatment methods available, these are considered in more detail below.

9.1 Combustion (flaring)

Flaring is used as a safety measure in the petroleum and chemical industries to quickly remove large quantities of flammable gases that may be generated or escape in an incident. It is also used to remove biogas generated by anaerobic water treatment processes. In this process, the flammable gases are directed to a torch with an appropriately designed burner incorporating a pilot flame and steam or air injection for good turbulence and mixing. A support fuel may also be necessary.

Gas from existing landfills may be treated by flaring if the volume or calorific content is not sufficient for energy utilisation. Systems are available from manufacturers such as Hofstetter (http://www.hofstetter.ch) and Marton Geotechnical Services Ltd (http://www.mgs.co.uk). However, these may not be capable of treating low volumes of gas from inorganic landfills.

Such methods have the advantages of:

- being a relatively cheap way to treat large quantities of solvent-loaded gases;
- can easily handle relatively large fluctuations in volume of gas produced.

But they have the disadvantages of:

- producing of NO_X, SO_X and other combustion products;
- not breaking down halogenated compounds;
- potentially creating light, noise, heat and odour nuisances;
- some incomplete combustion resulting from cooling at the flame edge.

The enclosed flares currently used to combust surplus landfill gas overcome some of these disadvantages by constraining the flame within the shroud. However, these devices are designed to use gas with a sustained, high-volumetric flow and relatively high calorific value. Some manufacturers have proposed flares with higher retention times (taller combustion zones), pre-heaters, pre-mixers and supplementary fuels.

However, the lower flash point of hydrogen compared with current landfill gas may present design problems for their application to future landfills.

9.2 Thermal post-combustion treatment

Following combustion, the gases are subjected to high temperatures (typically 750–1,200°C) in the presence of oxygen to encourage oxidisation. Most compounds can be broken down by this method; the efficiency of the process is dependent on the temperature, residence time, mixing and availability of oxygen.

Advantages include the high destruction efficiencies possible, but such methods have the following disadvantages:

- significant fuel costs may be required to maintain temperatures;
- halogenated and sulphur-containing gases will break down to aggressive acid gases;
- current technology is geared towards treatment of hydrocarbon gas streams.

Systems based on this technology for treating low calorific value landfill gas are available. These pass the residual gas and excess air through a hot ceramic matrix to oxidise the organic compounds. The VocsiBox® supplied by HAASE (http://www.haase-energietechnik.de/en), for example, can treat gas with 1 per cent residual methane using a packed bed of hot ceramic spheres at about 1,000°C. The unit is designed to operate autothermally but, if auxiliary firing is necessary, a gas such as propane may be used. In the post-combustion CL.AIR®-system used on Jenbacher gas engines, the exhaust gas flows over hot ceramic at approximately 800°C to oxidise uncombusted components of the exhaust gas (http://www.gepower.com). In both VocsiBox® and CL.AIR®, self-sustaining thermal oxidation is achieved by regularly reversing the flow to retain the exothermic reaction zone within the device. Computer control increases the complexity of the system.

Plasma arc devices have been used for complete oxidation of hazardous wastes and gases; see, for example, PLASCON™ produced by SRL Plasmal Ltd (http://www.srlplasma.com.au). However, these are expensive and their use may not be justified.

9.3 Catalytic post-combustion treatment

Catalytic post-combustion works in a similar way to thermal post-combustion but, following combustion, the off-gases are passed over a catalyst allowing oxidation to take place at a much lower temperature (approximately 300–500°C).

The choice of catalyst depends on the nature of the off-gases produced. For example, chromium/alumina or copper oxide/manganese oxide catalysts are selected for chlorinated compounds. For sulphur compounds, a platinum-based catalyst is usually selected, but these are quickly deactivated by the presence of chlorine. Other catalyst inhibitors include sulphur and zinc. Possible catalyst poisons include phosphorus, bismuth, arsenic, antimony, lead, mercury, iron, tin and silicon.

For catalytic post-combustion treatment to be effective for the treatment of landfill gas, the composition of the gas would have to be well-characterised to allow correct selection of catalyst and avoid deactivation by other compounds. Current experience with catalytic converters on landfill gas engines indicates that the trace components rapidly deactivate the commonly used catalysts.

The advantages of catalytic post-combustion compared with thermal post-combustion include:

- less fuel is required to support oxidation so running costs are likely to be lower;
- the equipment is more compact;
- reduced NO_X production.

However, it has the following disadvantages:

- risk of deactivation of catalyst through inhibitors or poisons;
- the current technology is geared towards disposal of VOC-loaded gas streams (e.g. from production of organic chemicals or polymers).

9.4 Wet scrubber: acid

Wet acid scrubbers are used in a variety of industries (e.g. pharmaceutical manufacturing, inorganic chemical manufacturing) and in foundries to treat off-gases as a stand-alone process, as a post-combustion treatment or in conjunction with another scrubbing method (e.g. an alkali scrubber).

Acid scrubbers work by bringing the gases into intimate contact with an aqueous acidic solution (e.g. through a packed bed column). Sulphuric acid solution is commonly used for economic reasons. Basic (alkali) gases react with the acid to form salts and some water-soluble gases are also dissolved into the solution.

This process is effective at removing ammonia (usually in a nitric acid scrubber), amines and esters. Sulphuric acid scrubbers can also absorb SO_X and nitric acid scrubbers can absorb NO_X.

The advantages of wet acid scrubbing include:

- used acid can be recovered, cleaned and reused,
- relatively compact system;
- can be built as modular multi-stage systems.

The disadvantages of wet acid scrubbing include:

- pH-specific contaminant removal;
- safety issues concerning the use of strong acid;
- a reactivity issue if landfill gas contains compounds such as phosphine/stibine/arsine;
- disposal of salts.

9.5 Wet scrubber: alkali

Alkali scrubbers operate in a similar manner to acidic wet scrubbers and are used across a variety of industries such as chlorine production and waste incineration. Acidic gases react with the alkali solution (e.g. a solution of sodium hydroxide) to form salts and some water-soluble gases can dissolve in the solution.

The main problem with an alkali scrubber is that insoluble carbonates are liable to form, which accumulate in the scrubber system causing blockages.

The advantages of wet alkali scrubbing include:

- relatively compact system;
- can be built as modular multi-stage systems.

The advantages of wet alkali scrubbing include:

- formation of insoluble carbonates;
- pH-specific contaminant removal;
- safety issues concerning the use of strong alkali;
- a reactivity issue if landfill gas contains compounds such as phosphine/stibine/arsine;
- disposal of salts.

9.6 Wet scrubber: alkali/oxidising

Similar again to the acidic and alkali wet scrubbers, alkali/oxidising scrubbers are used in the cosmetics industry, the food industry, in fertiliser production and in the textile industry for removal of fragrances and odours.

Organic odour compounds are oxidised in an alkaline environment using strong oxidants such as sodium hypochlorite or potassium permanganate. If hypochlorite is used as the scrubber liquor, chlorides are formed as a by-product, making this inappropriate for use with amine-containing gas streams. Manganese dioxide is formed as a waste by-product from the use of potassium permanganate scrubber liquors. Hydrogen peroxide does not form problematic by-products and is a possible alternative scrubber liquor, but it is a weaker oxidising agent than permanganate.

High removal efficiencies are possible with an alkali/oxidising scrubber; removal efficiencies are dependent on the oxidising strength of the scrubber liquor and the residence time in the scrubber – the longer the residence time required, the larger (and hence more expensive) scrubber installation is required.

The advantages of wet alkali/oxidising scrubbing include:

- removal efficiencies of up to 95 per cent are possible.

The disadvantages of wet alkali/oxidising scrubbing include:

- safety aspects concerning the use of a strong oxidising agent;
- specialist design of the installation is required.

9.7 Wet scrubber: solvent

Proprietary organic solvents are available to treat raw landfill gas (methane-based) prior to its use in landfill engines (Environment Agency 2004c). These systems have been developed to reduce the concentration of carbon dioxide, hydrogen sulphide and some other contaminants in methane-based landfill gas to improve its use as a fuel in landfill gas engines. While these particular systems will not be appropriate for use with a hydrogen-based landfill gas stream, the technology could be adapted to reduce some of the contaminants prior to flaring, for example.

The advantages of solvent scrubbing include:

- high affinity for acid gases (particularly carbon dioxide).

The advantages of solvent scrubbing include:

- current technology is unlikely to be appropriate for treatment of projected future landfill gas streams.

9.8 Wet scrubber: water

The basis of these processes is high pressure scrubbing of the gas streams with pressurised water (Environment Agency 2004c).

The advantages of wet scrubbing with water include:

- removes a significant proportion of acid gas contaminants (including carbon dioxide);
- contaminants can be released from wash water allowing recirculation and reuse.

The disadvantages of wet scrubbing with water include:

- high power consumption associated with pumping and handling of circulating flows.

9.9 Adsorption: activated carbon

Activated carbon is a microporous, inert carbon matrix, with a very large internal surface which is ideal for adsorption. Specialist treatment of the carbon to produce certain pore structures allow specific adsorptive capabilities to be obtained.

This flexibility in adsorptive capability means activated carbon can be used for gas purification across a very diverse range of industries from cleansing of process gases including hydrogen and natural gas, to recovery of perchloroethylene vapours in dry cleaning, and removal of dioxins and heavy metals from waste incinerator off-gases.

The gas flow is directed through the finely-divided activated carbon and the contaminants are adsorbed and bound to the activated carbon until it reaches saturation. The carbon can then be regenerated (usually by the supplier) and reused.

Further treatment capabilities for gases that are difficult to capture in a normal activated carbon bed are possible through the use of impregnated activated carbon. Here the pollutants are held in the carbon long enough to allow them to react with the chemical impregnation.

A variation on activated carbon adsorption treatment is the use of ‘Sorbalite’ (activated carbon and lime). This mixture is used for cleaning the off-gases from combustion ovens, allowing the removal of dioxins and SO_X compounds by one filter.

The advantages of activated carbon adsorption include:

- simple and robust technology;
- easy to put in place;
- easy to maintain;

- carbon can be regenerated and reused.

The advantages of activated carbon adsorption include:

- blockage of carbon can occur due to unexpected contaminants;
- not suitable for use with wet gas streams;
- risk of spontaneous combustion (e.g. reaction of ketones with activated carbon).

9.10 Adsorption: specialist zeolite (molecular sieves)

Zeolite is an aluminium silicate that occurs naturally and is also produced synthetically to meet certain specifications. The method of use is similar to that of activated carbon, with contaminants adsorbing into the pores in the three-dimensional structure. However, unlike activated carbon, zeolites are not usually regenerated and reused due to cost.

Zeolites are good adsorbers of polar substances (e.g. water and water-soluble substances), but can be synthesised to adsorb non-polar substances such as organic solvents.

The advantages of zeolite adsorption include:

- simple and robust technology;
- easy to put in place;
- easy to maintain.

The advantages of zeolite adsorption include:

- blockage of the zeolite can occur due to unexpected contaminants
- risk of fire in the bed (e.g. reaction with ketones)

9.11 Operational Issues

Treatment of gases from landfills containing predominantly inorganic residues will involve much lower volumes of gas than currently produced at MSW landfills. The flow will be less predictable and the calorific value may be inadequate to sustain the current design of landfill gas flare.

However, the gas may have a lower flash point and high diffusivity due to the higher concentration of hydrogen in the gas that is produced. This may require careful design of any gas control and collection system.

The advantage of a thermal treatment is that the main gases – hydrogen and methane – are converted to benign compounds. However, the combustion products will contain inorganic residues, which may be harmful if not adequately dispersed or collected.

Scrubbing and sorption systems may be useful to remove minor components, perhaps prior to a thermal treatment. However, the volume and hazard of the secondary wastes arising from scrubbing will be a consideration if these processes are used to sorb all the gaseous emissions.

10 Conclusions

10.1 Overall nature of gas

It is likely that the bulk gases (methane, carbon dioxide, hydrogen) released from inorganic landfills will be similar to those from existing mixed landfills. However, the relative amounts of these are expected to be different.

The main reason for this is that the generation of gases from microbial processes is likely to be slower than from an existing mixed waste landfill because of the smaller amount of degradable material, the absence of putrescibles, smaller microbial inocula and the more aggressive conditions. Thus hydrogen from corrosion is likely to form a greater percentage of the evolved gas and other trace components may become more important in assessments of gas release from future landfills.

A number of trace inorganic or organometal(loid) species have been identified as being generated from existing landfills or having the potential to be generated from future landfill accepting predominantly inorganic wastes.

Species may be generated from chemical or microbial action. The resulting gas composition will be dependent on:

- the nature of the waste;
- local and overall chemical and microbial conditions within the waste cell.

Interactions with the engineered components of the landfill, the surrounding soil, rock and groundwater, and ultimately the air, can influence the amounts of some gases released to the atmosphere.

Figure 10.1 provides a schematic diagram of the general processes of generation and consumption of volatile species in and around a landfill cell. Figures 10.2 and 10.3 illustrate this for a mixed waste landfill under anaerobic conditions and an aerobic inert waste landfill respectively. A comparison of the two diagrams shows the potential complexity of overall gas released from mixed waste compared with that from inert waste.

10.2 Information gaps

The study has highlighted the lack of data necessary to develop a full understanding of the evolution of trace gases from inorganic landfills.

Approaches developed for the treatment of gas from radioactive waste repositories can be applied to the generation of bulk gas from inorganic landfills. However, a better description of the waste inputs in terms of the chemical composition would be required. This is also true of components that may evolve trace gases.

In addition, the mechanisms and rates of trace gas generation need further consideration. Hirner (2003) notes that '… contents and emission potentials of special wastes like industrial or electronic waste have never been analysed for organometal(loid) compounds'.

The techniques for characterising wastes or contaminated soils do not normally measure the amount of available (zero valent) metal, yet this is an important determinant of the potential gas production from some important inorganic waste types.

A better characterisation of waste inputs to a landfill (or landfills), coupled with programmes to determine evolved gases from a well-characterised landfill where the waste inputs are known, would be of value.

It is also possible that gas sampling from old mixed sites where significant landfill gas production has ceased might provide useful data on trace species. The work on gaseous mercury reported by Lindberg *et al.* (2005) illustrates the need to take account of the types of waste disposed of, the physical nature of the landfill and the age of the landfill when considering the release of alkylated metal(loid) species.

Preliminary calculations have shown that it could take about 160 days for anaerobic conditions to be established in a capped conceptual mixed hazardous waste landfill by bare metal corrosion under unsaturated conditions. The rate of corrosion, and thus the onset of anaerobic conditions, will depend on the surface area of mild steel assumed in the calculations. For a low surface area (i.e. massive steel rather than thin metal sheet representing the same total amount of iron), anaerobic conditions may not be achieved. Protective coatings (e.g. paint) or encasement in an impermeable matrix (e.g. a silicate mass) could have a similar but unquantifiable effect. The results of the calculations are also sensitive to the properties of the cap; anaerobic conditions may not be achieved with a ‘less-tight’ cap. Calculations for a water-saturated landfill show conditions could become anaerobic more rapidly even at shallow depths.

10.3 Monitoring and treatment techniques

Analytical methods of sufficient sensitivity exist for all the species likely to be of interest in gas emissions from future landfills containing waste with higher concentrations of inorganic materials than existing landfills. Portable monitors offer some possibilities for monitoring species such as hydrogen at levels of interest. However, they may not be sensitive enough to measure the concentration of some other trace species.

‘Hyphenated’ laboratory analytical techniques (e.g. GC-ICP-MS) coupled with cryogenic trapping and cryofocusing appear capable of analysing a range of volatile trace species at very low concentrations.

It is likely that gas from future landfills containing low amounts of degradable organic materials and a high proportion of inorganic material including zero valent metal, will have the following characteristics.

- The main constituent will be hydrogen.
- It will also contain hydrogen sulphide, carbon dioxide, carbon monoxide, methane and NO_X.
- Trace gases will include hydrogen cyanide, hydrogen halides, metal carbonyls, ammonia, amines, carbon disulphide, phosphine, arsine and stibine.

Potential methods for treating such a landfill gas stream include thermal processes or scrubbing. Existing landfill gas flares are not adequate to deal with the low volumes of mixed gases likely to be produced by landfilled inorganic waste. Thermal processes will remove the combustible gases but will result in emission of inorganic species. Scrubbing will not treat all the gaseous components and will generate significant secondary wastes.

10.4 Future needs

The two most important needs that emerge from this study are:

- better characterisation of the waste inputs to landfills;
- gas data from the monitoring of sites known to have accepted wastes typical of those expected to be landfilled in the future.

The waste inputs need to be better characterised in terms of the types of materials being sent for disposal and their chemical composition including, for some elements, knowledge of their oxidation state. For instance, it is important to know whether the amounts of iron and aluminium present are in the zero valent state (i.e. as the metal), as corrosion of the metals generates hydrogen.

Monitoring is necessary to identify whether species of concern are being produced. Initially, trace volatile elements should be identified. Once this has been achieved, analysis should focus in more detail on the speciation of these identified elements of most concern. In addition, speciation information will give an indication of the processes occurring in the landfill. It is important that bulk gas is sampled contemporaneously for analysis with samples obtained for trace analyses.

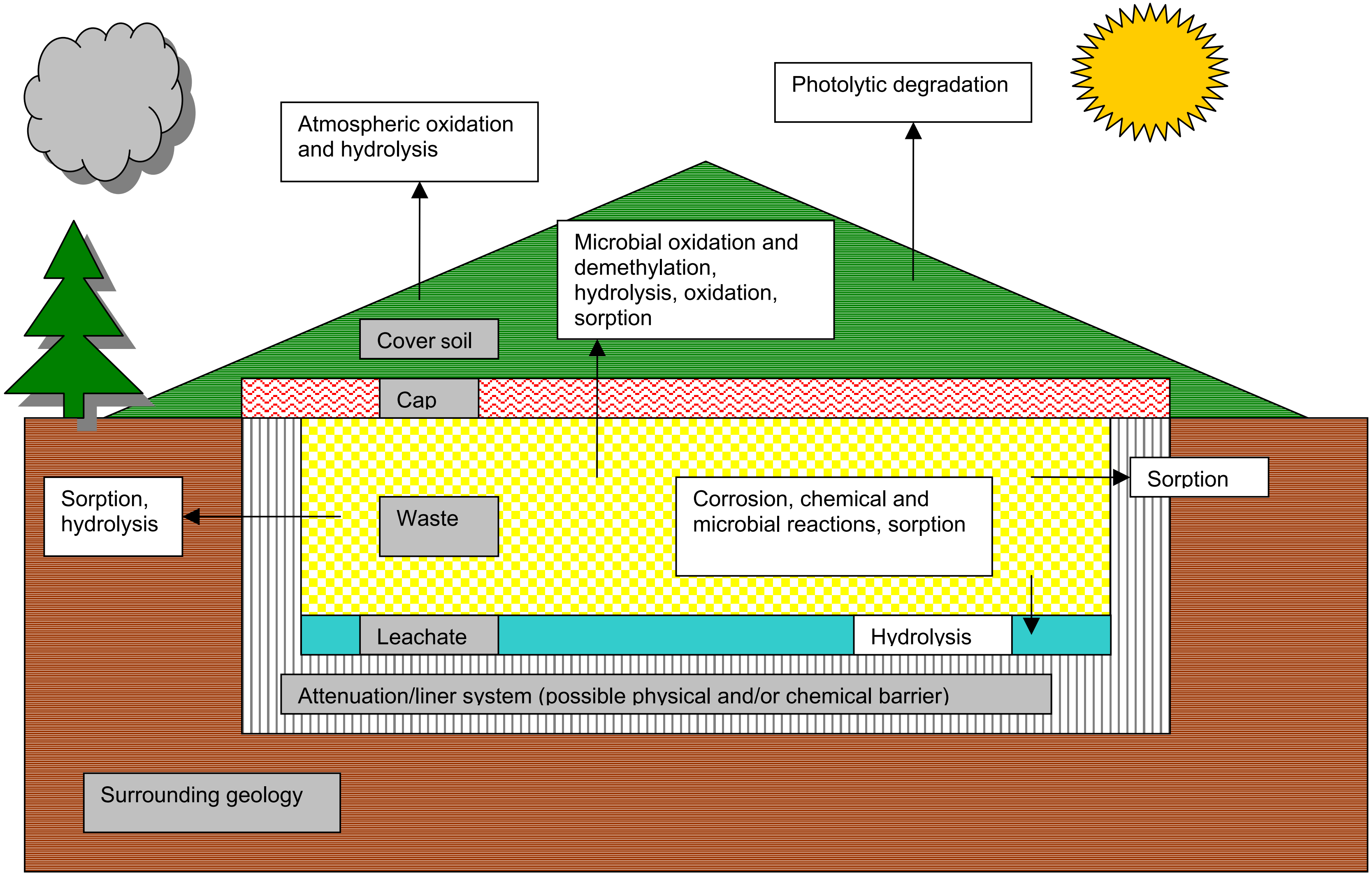


Figure 10.1 Regions of a landfill and general generation and consumption processes for volatile species

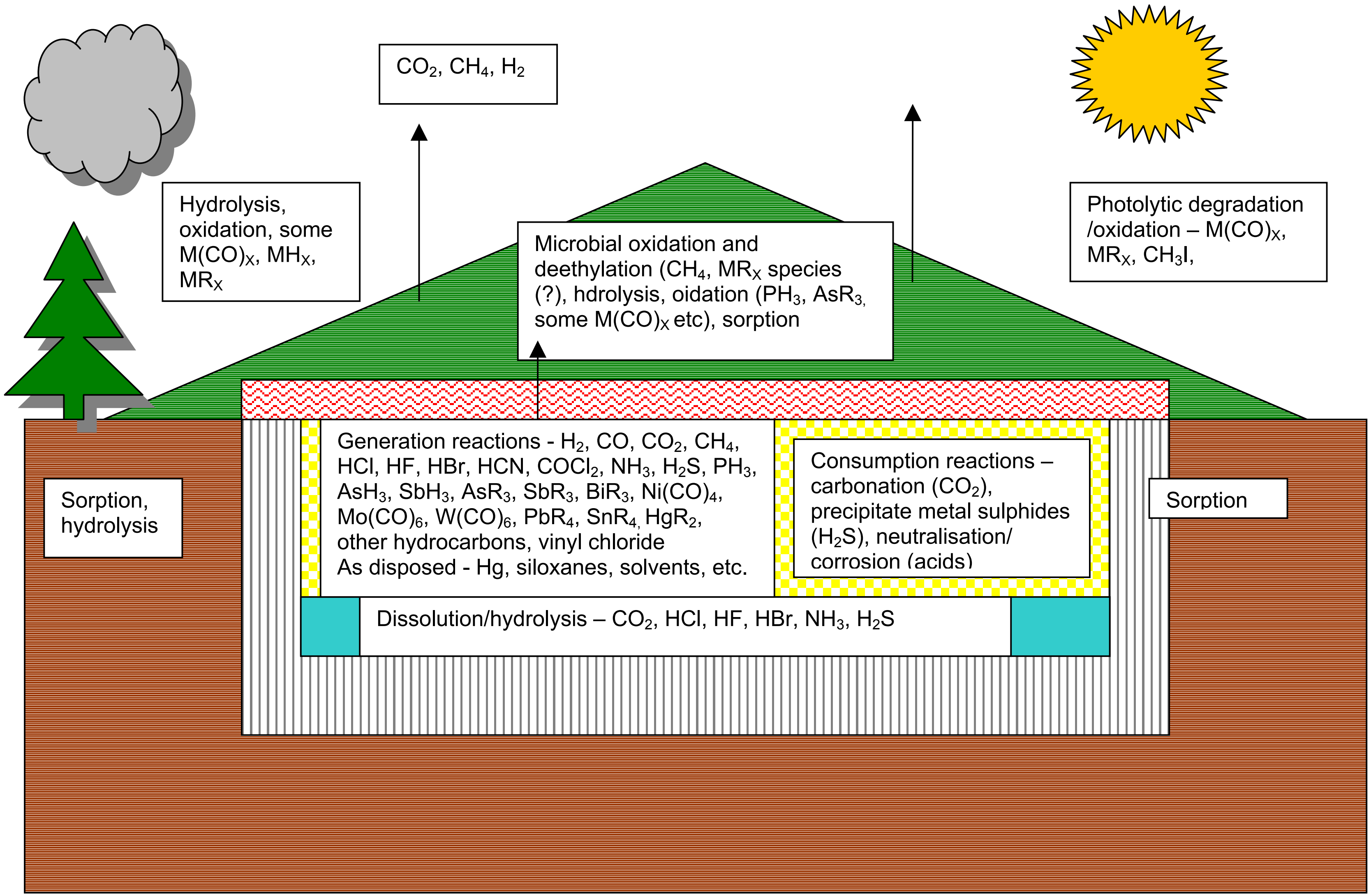


Figure 10.2 Principal products and reactions – mixed waste, anaerobic, microbial action

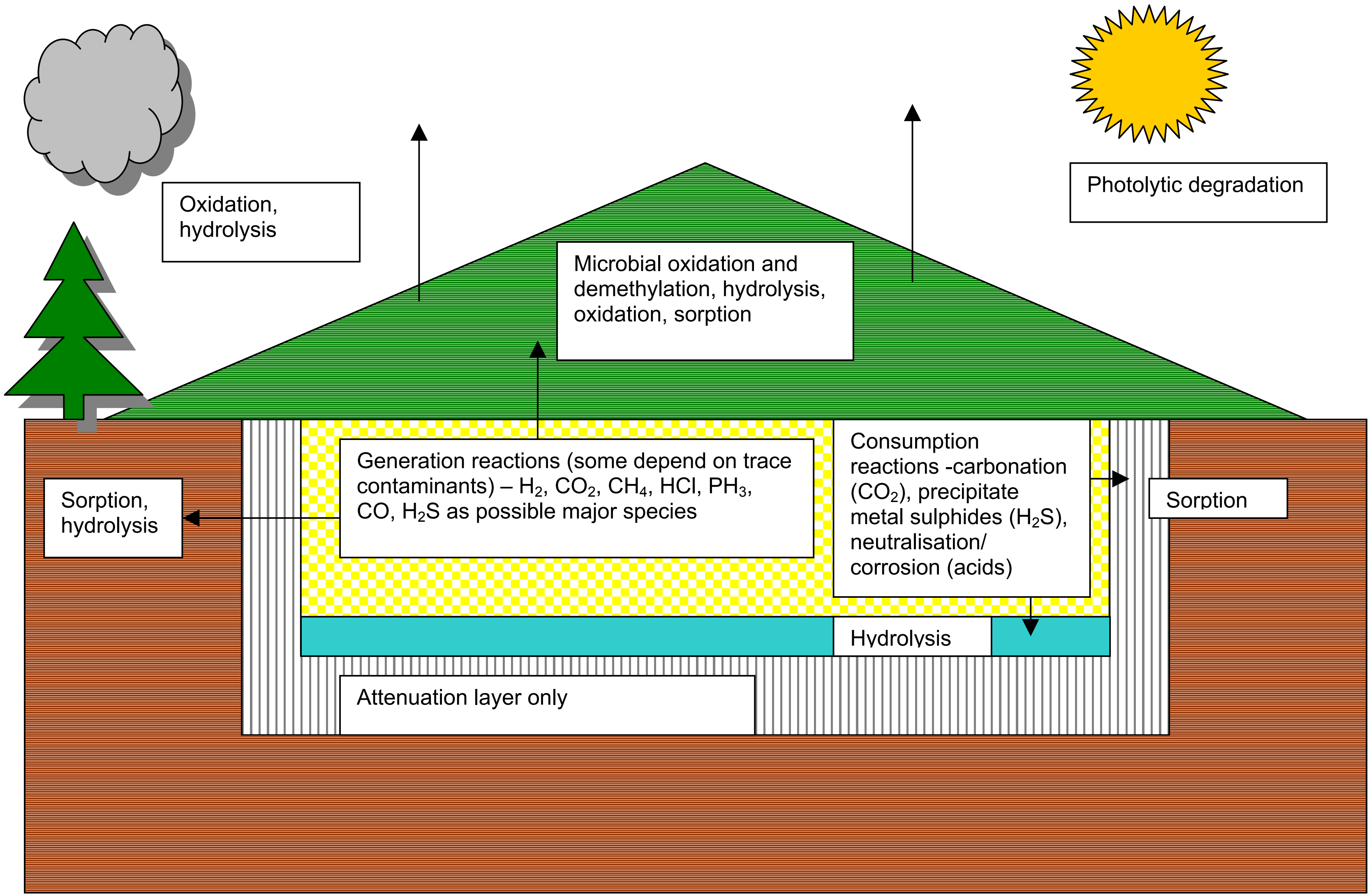


Figure 10.3 Principal products and reactions – inert waste, aerobic, very limited microbial action

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List of abbreviations

AAS	atomic absorption spectroscopy
AES	atomic emission spectroscopy
AFS	atomic fluorescence spectroscopy
APC	air pollution control
ASL	Approved Supply List
ATD	automated thermal desoprtion
C&D	construction and demolition
CDEW	construction, demolition and excavation waste
C&I	commercial and industrial
CV-AAS	cold vapour-atomic absorption spectroscopy
CV-AES	cold vapour-atomic emission spectroscopy
ELV	End of Life Vehicle
ETAAS	Electrothermal atomic absorption spectroscopy
EWC	European Waste Catalogue
GC	gas chromatography
GC-MS	gas chromatography-mass spectrometry
HG	hydride generation
HHW	hazardous household waste
HPLC	high performance liquid chromatography
ICP-AES	inductively coupled plasma-atomic emission spectroscopy
ICP-MS	inductively coupled plasma-mass spectrometry
IR	infrared
LOD	Limit of Detection
LTWEL	Long-Term Workplace Exposure Limit
MS	mass spectrometry
MSW	municipal solid waste
NIOSH	National Institute of Occupational Safety and Health
PCDDs	polychlorinated dibenzo-*p*-dioxins
PCDFs	polychlorinated dibenzofurans
ppb	parts per billion
ppm	parts per million

PPC	Pollution Prevention and Control
PVC	Polyvinylchloride
SNRHW	Stable Non-reactive Hazardous Waste
SRB	sulphate-reducing bacteria
UV	ultraviolet
USEPA	US Environmental Protection Agency
VOCs	volatile organic compounds
WAC	Waste Acceptance Criteria

Glossary

ATD tubes	Automated thermal desorption tubes used for sampling from the gas phase.
Gresham tube	A proprietary design of sampling equipment that can be used to collect gas samples. It comprises an empty metal tube, valves and hand pump.
Tedlar bag	A bag constructed of inert material (polyvinyl fluoride) for taking gaseous grab samples
XAD	A proprietary ion exchanger comprising beads of cross-linked polystyrene.

Appendix A: Methodology for estimating future composition of wastes in main classes of landfill

Landfill data from 2002 in the Environment Agency's Hazardous Waste Interrogator (Environment Agency 2005a) were used as the starting point in developing the conceptual model landfill inventories. Data on the quantities of waste by European Waste Catalogue (CEU 2002) chapter/category were gathered and the types of wastes contained within the EWC categorisation assessed.

The next step was to determine the disposal routes and likely quantities of these wastes from 2005 onwards. The following were taken into account:

- regulatory changes such as the change from Waste Management Licensing to PPC permitting;
- the effects of the Landfill and Hazardous Waste Directives;
- social/political factors such as the increasing drive towards recycling and reuse of wastes;
- economic factors (e.g. increased disposal charges to waste consignors), particularly in relation to disposal at hazardous waste landfills.

Where an EWC category was marked as an absolute (A) hazardous entry, those waste streams were generally assumed to go to hazardous landfill.

Where the EWC category was marked as a mirror (M)7 hazardous entry, the waste streams were split into hazardous and non-hazardous streams with judgement applied to the relative split.

Where the EWC category carried no marking, those waste streams were assumed to go to non-hazardous landfill.

The exceptions to this general process were the 11 non-hazardous EWC categories specified in the Interim Waste Acceptance Criteria (Environment Agency 2002) which can be accepted into inert sites without testing. It was assumed that these waste streams would go to inert landfill with very little routed to non-hazardous landfill due to the expected differences in overall costs of disposal. A small amount of these wastes was assumed to go to other landfill types for use as landfill construction materials. in addition, hazardous asbestos-containing wastes and gypsum wastes were assumed to go to monofilled cells at non-hazardous sites. Finally, it was assumed that tar waste streams (e.g. 05 06 03 other tars) would be sent for incineration and that the resulting ash would be disposed of as monofill.

The likely change in quantity of each waste category going to landfill disposal was estimated. These estimates took into account factors such as:

- the unsuitability of certain waste types under the new WAC;
- increased and emergent recycling techniques;

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7 Absolute entries – hazardous waste regardless of any threshold concentrations; Mirror entries – hazardous waste only if dangerous substances are present above threshold concentrations (Environment Agency 2003a).

- the requirement to pre-treat and reduce the volume of wastes before disposal to landfill.

Account was taken of the efficiency of recycling to recover items from mixed waste streams. Although aluminium – and to an extent iron – have significant value, for instance, finely divided, contaminated and occluded material will pass though typical sorting systems.

Economic considerations were also taken into account by assuming that, in general, landfilling of wastes (particularly hazardous waste) from 2005 onwards would be significantly more expensive than it had been in 2002, encouraging waste producers to look to alternative means of disposal. On the whole, the levels of waste disposed at landfill were judged to fall from the amounts in 2002. However, some waste streams (e.g. fragmentiser wastes from ELV processing) were judged likely to show an increase from their 2002 quantities due to the impact of other waste legislation.

An estimate of the overall composition of each model mixed waste landfill inventory is required in order to consider its potential for bulk gas generation. An estimate of the proportions of the likely major components in each stream was therefore made. The typical composition and per cent weight contribution of any packaging (e.g. steel or plastic drums) were also estimated where relevant.

These estimates of composition were based on knowledge and experience of typical waste streams supported by reference to:

- internet resources (Environment Agency 2005b, ESA 2005, NZME 2005);
- the Approved Supply List (ASL) (HSE 2002);
- some discussion with waste organisations.

The estimated masses of the waste stream components were assigned to generic categories based on:

- their expected gas generating behaviour or potential to produce volatile compounds of interest;
- their possible effect on the chemical environment within the landfill.

This classification was based on general chemical knowledge. The components of the wastes were assigned to the following categories:

- iron and steel;
- aluminium as metal;
- zinc as metal;
- cements and alkaline solids;
- recalcitrant organic material (e.g. synthetic polymers other than PVC);
- oils;
- other non-halogenated organic compounds and residues;
- halogenated solvents and residues;
- PVC;
- wood, paper and cardboard;
- other inorganic chemicals and other materials;

- inert materials ('inert' in terms of their potential for gas production only, not inert wastes as defined in interim WAC);
- lead.

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Appendix B: Xenobiotic compounds and heavy metals frequently found in MSW and co-disposal leachates with a possible origin in household hazardous waste

Tables B1 and B2 are taken from Slack *et al.* (2005) and list:

- xenobiotic compounds found in leachates from MSW and co-disposal landfills that may have a possible origin in household hazardous waste (HHW) from domestic sources;
- ranges of heavy metal concentrations detected in landfill leachates.

Domestic waste represents over two-thirds of MSW and HHW is landfilled with general household waste. Slack *et al.* (2005) note other studies have found that, even without landfill co-disposal, leachates from MSW are very similar in composition to those from mixed or hazardous landfills.

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Table B1 Xenobiotic compounds frequently found in MSW and co-disposal landfill leachates with a possible origin in HHW[1]

Compound	CAS no.	Use	Presence in HHW[2]	Landfill type and reference[3]
Halogenated hydrocarbons				
Bromodichloromethane	75-27-4	Chlorinated water, some as manufacturing substrate	X	2
Chlorobenzene	108-90-7	Industrial solvent and substrate	X	1,3,5,8,15
1,4-Dichlorobenzene	106-46-7	Toilet deodorisers and mothballs	Y	1,3,5,7,8
1,3-Dichlorobenzene	541-73-1	Insecticide/fumigant; chlorophenol substrate	X	1,7,8
1,2-Dichlorobenzene	95-50-1	Pesticide, manufacturing substrate, deodoriser, solvent	Y	1,3,5,7,8,15
1,2,3-Trichlorobenzene	87-61-6	Insecticide, substrate, solvent	X/Y	1,2,7
1,2,4-Trichlorobenzene	120-82-1	Insecticide, substrate, solvent	X/Y	1,2,7,8
1,3,5-Trichlorobenzene	108-70-3	Chemical intermediate, explosives, pesticides	X/Y	2
Hexachlorobenzene	118-74-1	Industrial by-product of solvent, pesticide and wood preservation	X	1
Hexachlorobutadiene	87-68-3	Manu. of rubber/lubricants and industry	X	2
1,1-Dichloroethane	75-34-3	Paint solvent, degreasant, breakdown of 1,1,1-trichloroethane	X/Y	1
1,2-Dichloroethane	107-06-2	Vinyl chloride manufacture: paint, adhesives, pesticides and cleaning products: solvent to remove petrol lead	Y(old)	1,2,7,8
Tribromomethane	75-25-2	Degreasant and substrate – no longer used	X	2
1,1,1-Trichloroethane	71-55-6	Solvent especially paint and adhesive; cleaning products and aerosols	Y	1,2,3,5
1,1,2-Trichloroethane	79-00-5	Solvent, unknown use; 1,1,2,2-tetrachloroethane breakdown product	X/Y	1
1,1,2,2-Tetrachloroethane	79-34-5	Industrial solvent and substrate; was used in paint, pesticides and degreasant	X/Y	1
trans-1,2-Dichloroethylene	156-60-5	Solvent and manufacturing (pharmaceuticals, etc.)	X/Y	1
cis-1,2-Dichloroethylene	156-59-2	Solvent (perfumes, etc.) and manufacturing. (pharmaceuticals, etc.)	X/Y	1

Table B1 (cont'd) Xenobiotic compounds frequently found in MSW and co-disposal landfill leachates with a possible origin in HHW[1]

Compound	CAS no.	Use	Presence in HHW[2]	Landfill type and reference[3]
Trichloroethylene	79-01-6	Solvent, substrate, degreasant: solvent in Tippex, paint removers, adhesives and cleaners	Y(old)	1,2,3,5,8
Tetrachloroethylene	127-18-4	Dry-cleaning and degreasant	X	1,2,3,5,8
Dichloromethane	75-09-2	Solvent in paint stripper, aerosols, cleaners, photographics, pesticides	Y(old)	1,5,7,8
Trichloromethane	67-66-3	Solvent and substrate: forms from Cl in water	X	1,5,7,8
Carbon tetrachloride	56-23-5	All uses stopped? No longer a refrigerant, etc. Used for plastics?	Y	1,2,8
Chloroethene	75-01-4	Plastics and vinyl production – house, drugs, etc.	Y	8
Aromatic hydrocarbons				
Benzene	71-43-2	Multitude of uses – manufacturing of dyes, pesticides, drugs, lubricants and detergents	Y	1,2,3,5,6,7,8,13, 15
Toluene	108-88-3	Solvent in paint, paint thinners, nail varnish, etc.	Y	1,2,3,5,7,8,13,15
Xylenes	1330-20-7	Plastics manufacture: solvent in paints, nail varnish	Y	1,2,3,5,6,7,8,13, 15
Ethylbenzene	100-41-4	Pesticides, varnishes, adhesives and paints	Y	1,2,3,5,8,13,15
Trimethylbenzenes	N/A	Solvent, substrate (paint, perfume dye), fuel	X/Y	1,3,5,8,13
n-Propylbenzene	103-65-1	Solvent and manufacture	X	1,8,13
t-Butylbenzene	98-06-6	Solvent and manufacture	X	1,8
Ethyltoluenes	e.g. 622-96-8	Solvent and manufacture	X	1,8,13
Naphthalene	91-20-3	Moth repellent, toilet deodoriser, manufacture of dyes and resins	Y	1,3,5,6,7,8,13,15
2-Methylnaphthalene	91-57-6	Insecticides, chemical intermediate (dye/vitamin K)	Y	3,7,8,13,15
1-Methylnaphthalene	90-12-0	Insecticides, chemical intermediate (dye/vitamin K)	Y	3,7,8,13,15
Phenols				
Phenol	108-95-2	Slimicide, disinfectant, drugs and manufacture	X/Y	1,2,3,5,6,7,12,13, 15

Table B1 (cont'd) Xenobiotic compounds frequently found in MSW and co-disposal landfill leachates with a possible origin in HHW[1]

Compound	CAS no.	Use	Presence in HHW[2]	Landfill type and reference[3]
Ethylphenols	90-00-6	Solvent, naturally occurring in some foods	X/Y	1,3,15
Cresols	1319-77-3	Wood preservatives, drugs, disinfectant and manufacture	Y	1,3,5.6,7,12,13, 15
Bisphenol a	As phenol	Manufacture of epoxy resins, coating on food cans?	Y	1,6,7,15
Dimethylphenols	105-67-9	Solvent	X(Y)	1,12,15
2-Meth/4-methoxyphenol	90-05-1/50-76-5	Manu. Antioxidants, drugs, plastics, dyes: flavouring	Y	1
Chlorophenols	95-57-8	Pesticides, antiseptics, manufacturing, Cl-treated water	X(Y)	1,7,12,13,15
2,4-Dichlorophenol	120-83-2	Manufacture of herbicides, PCP: mothballs, disinfectant	Y	7
3,5-Dichlorophenol	591-35-5	Manu. Herbicides, PCP; mothballs, disinfectant	Y	1
Trichlorophenols	N/A	PCP and organochlorine pesticide metabolites	X/Y	15
2,3,4,6-Tetrachlorophenol	58-90-2	Pesticides, wood preservative	X	1,15
Pentachlorophenol	87-86-5	Wood preservative no longer used in households	Y(old)	2,15
Polychlorinated biphenyls	1336-36-3	Transformers and capacitors: <1970s used in consumables paint, adhesives, fluorescent lamps, oil, WEE	X	2
Alkylphenols				
Nonylphenol	104-40-5	Surfactants	X/Y	1,15
Nonylphenol ethoxylate	9016-40-9/NA 31	Detergents, wetting/dispersing agents, emulsifier	X/Y	15
Pesticides				
Aldrin/dieldrin	309-00-2/60-57-1	Banned insecticides	X	2
Ametryn	834-12-8	Herbicide	X	1
Ampa	N/A	Glyphosate	X	1
Atrazine	1912-24-9	Herbicide – US licensed	Y	2,7
Bentazon	25057-89-0	Herbicide	X	1
Chloridazon	1698-60-8	Pyridazinone herbicide	X	1
Chlorpropham	101-21-3	Carbinilate herbicide	X	1
DDT (DDD, DDE)	50-29-3 (72-54/55-8/9)	Banned insecticides	X	2
Dichlobenil	1194-65-6	Herbicide	Y	1

Table B1 (cont'd) Xenobiotic compounds frequently found in MSW and co-disposal landfill leachates with a possible origin in HHW[1]

Compound	CAS no.	Use	Presence in HHW[2]	Landfill type and reference[3]
Dichlorvos	62-73-7	Insecticide (indoor) and veterinary care	Y	2
N,N-Diethyltoluamide	134-62-3	Insecticide (body)	Y	6
Endosulfan (α/β)	33213-65-9	Insecticide and wood preservative	X	2
Endrin	72-20-8	No longer used (insect/rodent/avicide)	X	2
Fenpropimorf	67564-91-4	Morpholine fungicide	X	1
Glyphosate	1071-83-6	Herbicide	Y	1
Hexazinon	512-350-42	Non-agricultural herbicide	X	1
Hydroxyatrazin	2163-68-0	Atrazine metabolite	X	1
Hydroxysimazin	NA 1063	Simazine metabolite	X	1
Isoproturon	34123-59-6	Phenylurea herbicide	X	1
γ-Hexachlorocyclohexane	581-89-9	Insecticide and lice treatment	Y	1,2
Malathion	121-75-5	Insecticide, flea and lice treatment	Y	2
Mecoprop	7085-18-0	Herbicide	Y	1,4,5,6,13,14
Methyl parathion	298-00-0	Insecticide – agricultural	X	2
MCPA	94-74-6	Herbicide	Y	1
Propoxur	114-26-1	Acaricide/insecticide	X	1
Simazine	122-34-9	Herbicide	Y	2
Tridimefon	43121-43-3	Fungicide	X	1
4-CCP	3307-39-9	Herbicide	X	1
2,4-D	94-75-7	Herbicide	Y	1
2,4,5-T	93-76-5	Herbicide (Agent Orange)	X	1
2,4-DP	120-36-5	Herbicide (alongside Mecoprop)	Y	1
Phthalates				
Monomethyl phthalate	-	Plastics	Y	1
Dimethylphthalate	-	Plastics	Y	1,7
Diethyl phthalate	84-66-2	All plastic consumables, insecticides, drugs, cosmetics	Y	1,4,5,6,7,9,15
Methyl-ethyl phthalate	-	Plastics	Y	1,9
Mono-(2-ethylhexyl) phthalate	-	Plastics	Y	1,9
Di-(2-ethylhexyl) phthalate	117-81-7	All plastics including medical ware	Y	1,6,7,9,10,15
Mono-butylphthalate	-	Plastics	Y	1,9
Di-*n*-butylphthalate	84-74-2	PVC plastics and nitrocellulose lacquers (varnish)	Y	1,5,6,7,9,15
Di-isobutylphthalate	-	Plastics	Y	1,6,9
Mono-benzylphthalate	-	Plastics	Y	1,9
Butylbenzyl phthalate	85-68-7	Plastics	Y	1,9,15
Dioctylphthalate	117-84-0	All plastics, pesticides and cosmetics	Y	1,6,15

Table B1 (cont'd) Xenobiotic compounds frequently found in MSW and co-disposal landfill leachates with a possible origin in HHW[1]

Compound	CAS no.	Use	Presence in HHW[2]	Landfill type and reference[3]
Phthalic acid	N/A	Phthalate breakdown product	Y	1,6,10
Diheptyl phthalate	3648-21-3	Plastics	Y	7
Aromatic sulphonates				
Naphthalene sulphonates	-	Azo dyes, detergents, plasticisers	Y	1
Benzene sulphonates	68411-30-3	Azo dyes, detergents, plasticisers	Y	1
p-Toluenesulphonate	80-4-0	Azo dyes, detergents, plasticisers	Y	1
Sulphones and sulphonamides				
Diphenylsulphone	127-63-9	Plasticiser and intermediates	Y	6
N-Butylbenzene sulphonamide	3622-84-2	Plasticiser	Y	6,15
Phosphonates				
Tributylphosphate	126-73-8	Plasticiser, solvent, antifoaming agent	Y	1,3,5,6,15
Triethylphosphate	78-40-0	Plasticiser, solvent, antifoaming agent	Y	1,3,6,7,15
Terpenoids				
Terpenoids (general)	N/A	Plant by-product, chemical intermediate	Y	11
Borneol	507-70-0	Chemical, perfume, flavouring intermediates	Y	6
Camphor	76-22-2	Perfume and incense additive	Y	1,3,5,6,8,13,15
1,8-Cineole	470-82-6	Flavours and fragrance	Y	3,6
Fenchone	e.g.1195-79-5	Flavouring	Y	1,3,6,13
Limonene	5989-27-5	Flavouring	Y	-
Menthol	15356-70-4	Flavours and fragrance	Y	3
Pinene	e.g. 80-56-8	Flavours and fragrance	Y	15
α-Terpineol	98-55-5	Flavours and fragrance	Y	6,7
Tetralins	N/A	Flavours and fragrance	Y	15
Thymol	89-83-8	Flavours and fragrance	Y	6
Pharmaceuticals				
Ibuprofen	15687-27-1	Anti-inflammatory/analgesic – over-the-counter (OTC)	Y	6
Propylphenazone				
Phenazone	479-92-5/60-80-0	Analgesic – rarely used today	X	6,15
Clofibric acid	882-09-7	Plant growth regulator and drug intermediate	Y	6
Pyridines				
Methylpyridine (2-?)	109-06-8	Solvent and substrate for dyes, resins , drugs	X	6
Nicotine	54-11-5	Insecticide, tobacco	X/Y	1,6
Cotinine	486-56-6	Formed from oxidation of nicotine	X/Y	6

Table B1 (cont'd) Xenobiotic compounds frequently found in MSW and co-disposal landfill leachates with a possible origin in HHW[1]

Compound	CAS no.	Use	Presence in HHW[2]	Landfill type and reference[3]
Carboxylic acids				
Benzoic acid	65-85-0	Food preservative, perfumes, creams/drugs, manufacturing	Y	3,6,15
Phenylacetic acid	103-82-2	Fragrance/flavour, drugs (penicillin)	Y	3,6
Benzenetricarboxyl acids	e.g. 528-44-9	Plastic softeners	Y	3,6
Palmitic acid	57-10-3	Food, cosmetics and pharmaceuticals	Y	3,6,15
Stearic acid	57-11-4	Food, cosmetics and pharmaceuticals	Y	3,6,15
Linoleic acid	60-33-3	Food and fragrance	Y	3,6
Aliphatics				
n-Tricosane	638-67-5	Plastics and intermediate	X	6,7
n-Triacontane	638-68-6	Intermediate	X	6,7
Alcohols and ethers				
Glycol ethers	e.g. 111-76-2	Solvent (paint, varnish, inks, pesticides, antifreeze)	Y	6
General alcohols	N/A	Solvents	Y	1
Diphenylethers	101-54-8	Flame retardant, plasticizer, herbicide	Y	6
Aldehydes and ketones				
Aldehydes	N/A	Solvents (plastics, paints)	Y	1,6
Ketones	N/A	Preservative, resin/dye manufacturing intermediate	Y	1,6
Miscellaneous				
Acetone	67-64-1	Solvent and in manufacture of plastics, drugs and fibres	Y	1
Analines	N/A	Ink/dye, resins, drugs, agrochemical intermediate	X/Y	3,6,7
Benzonitrile	100-47-0	Solvent: dye, drugs, rubber, lacquer manufacture	Y	3,4,7,15
Benzthiazoles	N/A	Manufacture of drugs, rubber, agrochemicals, etc.	Y	6,7
Dibenzofuran	13-26-49	From fossil fuel combustion – including diesel fuel	X	7
Caffeine	58-08-2	Food additive, drugs	Y	1,7
Esters	110843-98-6	Many uses during manufacture	Y	6,15
Tetrahydrofuran	109-99-9	Food additive, reagent (drugs, perfumes), solvent	Y	1

Table B1 (cont'd) Xenobiotic compounds frequently found in MSW and co-disposal landfill leachates with a possible origin in HHW[1]

Compound	CAS no.	Use	Presence in HHW[2]	Landfill type and reference[3]
Indane	90989-41-6	Fuel and metal cleaning	Y	1,6
Indene	95-13-6	Solvent and intermediate	Y	8
Indoles	N/A	Intermediates, food colourant, drugs/ hallucinogenics, perfumes, etc.	Y	6,15
MTBE	1634-04-4	Solvent used as additive in unleaded petrol	X(Y)	1
Siloxanes	N/A	Silicone polymers – varnish, oils/waxes, rubber	Y	6,15
Styrene	100-442-5	Naturally occurring, used for plastics/rubber manufacture	Y	8,15
Trifluralin	158-20-98	Herbicide	X	2

Notes:

[1] Slack *et al.* (2005)

[2] Presence in HHW:
X = non-municipal/household use; Y = municipal/household use;
X/Y = either/or but generally non-municipal/household use;
X(Y) = non-municipal/household but possibly occurring in MSW;
Y(old) = no longer used in municipal/household products but possibly occurring in MSW.

[3] Landfill types (as referenced in Slack *et al.* 2005):
1 = co-disposal landfills;
2 = MSW landfills although co-disposal likely in all;
3 = co-disposal landfills;
4 = simulation using household waste;
5 = co-disposal landfill;
6 = no details supplied;
7 = co-disposal landfill;
8 = co-disposal landfill;
9 = mixed landfills receiving different wastes;
10 = simulation using household waste;
11 = MSW landfill;
12 = co-disposal landfill;
13 = co-disposal landfill;
14 = co-disposal landfill;
15 = co-disposal landfill.

Table B2 Heavy metal concentration ranges detected in landfill leachates[1]

Metal	Use	Concentration range (mg dm^{-3})
Cadmium	Batteries, appliances	0.0001–0.04
Nickel	Batteries, appliances	0.0036–13
Zinc	Batteries, packaging	0.003–1000
Copper	Electrical appliances	0.002–10
Lead	Batteries, appliances	0.001–5
Chromium	Electrical appliances	0–1.62
Mercury	Batteries, appliances	0.00005–0.16
Arsenic	Appliances	0.01–1
Cobalt	Appliances	0.005–1.5

Notes: [1] Slack *et al.* (2005)

Appendix C: Thermodynamic data and susceptibility to oxidation for a number of methyl and hydride species

Table C1 Standard molar enthalpies of formation for $(CH_3)_nM$ compounds of environmental interest[1]

Element	ΔH_f (kJ mol^{-1})[2]
Group III (n = 3)	
B	–122
Al	–88
Ga	–39
In	+172
Tl	–
Group IV (n = 4)	
C	–167
Si	–238
Ge	–71
Sn	–19
Pb	+137
Group V (n = 3)	
N	–24
P	–96
As	+15
Sb	+31
Bi	+192
Group VI (n = 2)	
O	+195
S	–
Se	–57[3]
Te	–
Po	–
Group IIB (n – 2)	
Zn	+55
Cd	+110
Hg	+93

Notes:

[1] Craig (1986). All the compounds can be isolated and stored at room temperature; some require inert atmospheres.

[2] ΔH_f is for formation from the elements at 298K and 1 atmosphere pressure, endothermic ΔH_f (positive) = exothermic decomposition.

[3] $(C_2H_5)_2Se$

Note that entropy plays an effect (i.e. $\Delta G_D = \Delta H_D - T\Delta S_D$), so $T\Delta S_D$ is large and negative. This renders exothermic compounds of slight stability even less stable than appears at first sight as ΔG_D becomes negative. Note also that kinetic factors may play a part (e.g. $Pb(CH_3)_4$ is stable because of kinetics); there is no decomposition route with a low activation energy.

Table C2 Mean bond dissociation energies (D_e) for $(CH_3)_nM$ compounds of environmental interest[1]

Element	D_e (kJ mol^{-1})[2]
Group III (n = 3)	
B	364
Al	276
Ga	247
In	163
Tl	–
Group IV (n = 4)	
C	347
Si	320
Ge	247
Sn	218
Pb	155
Group V (n = 3)	
N	314
P	276
As	230
Sb	218
Bi	141
Group VI (n = 2)	
O	358
S	289
Se	247
Te	–
Po	–
Group IIB (n – 2)	
Zn	176
Cd	138
Hg	123

Notes:

[1] Craig (1986)

[2] D_e values are mean values required to break one mole of bonds homolytically at ideal gas state at 1 atmosphere and 298.15K, i.e. $R_nM(g) \rightarrow M(g) + nR\cdot(g)$; $\sum de / n = D_e$

In general, bond strength decreases as a group is descended.

Those organometallic compounds, which are not met in the environment, are often unstable for reasons other than thermal instability at normal temperatures.

Table C3 Stability of methylmetals to oxygen at room temperature[1]

Stable[2]	Unstable
$(CH_3)_2Hg$	$(CH_3)_2Cd$
$(CH_3)_4Si$	$(CH_3)_3M$ (M = B, Al, Ga, In, Tl)
$(CH_3)_4Ge$	$(CH_3)_3M$ (M = As, Sb, Bi)
$(CH_3)_4Sn$	$(CH_3)_2AsH$
$(CH_3)_4Pb$	CH_3AsX_2
$(CH_3)HgX$	CH_3SbX_2
$(CH_3)_{4-n}SnX_n$	$(CH_3)_{4-n}SnH_n$
$(CH_3)_3PbX$	
$(CH_3)_2PbX_2$	
$(CH_3)_2S$	
$(CH_3)_2Se$	

Notes: [1] Craig (1986)
[2] Stable against rapid oxidation over a timescale of seconds to minutes.

In general, there is an increasing susceptibility to oxidation as a main group is descended. Assume that ethyl compounds would be less stable than methyl.

General comments on stability against hydrolysis:

- R_2Hg, R_4Sn, R_4Pb = only slightly soluble, stable, diffuse to atmosphere. Higher alkyls less and less volatile
- $(CH_3)_2As^+$, $(CH_3)_3Pb^+$, $(CH_3)As^{2+}$ = hydrolyse

Table C4 Standard molar enthalpies of formation for H_nM compounds of environmental interest[1]

Element	ΔH_f (kJ mol^{-1})
Group III (n = 3)	
B	+100.0
Al	–
Ga	–
In	–
Tl	–
Group IV (n = 4)	
C	–74.4
Si	+34.3
Ge	+90.8
Sn	+162.8
Pb	–
Group V (n = 3)	
N	–45.9
P	+5.4
As	+66.4
Sb	+145.1
Bi	–
Group VI (n = 2)	
O	–241.8
S	–20.6
Se	+29.7
Te	+99.6
Po	–

Notes: [1] Lide (1994). 298.15K and 100kPa (1 bar); all as gas unless otherwise stated.

Table C5 Standard molar enthalpies of formation for some other compounds of environmental interest[1]

Species	ΔH_f (kJ mol^{-1})
$Ni(CO)_4$	–602.9 (g), –633.0 (l)
$Fe(CO)_5$	–774(l)
$Mo(CO)_6$	–912.1 (l), –982.8 (s)
SF_6	–1220.5
CH_3I	+14.7

Notes: [1] Lide (1994)

References

Craig P J (1986) Occurrence and pathways of organometallic compounds in the environment – general considerations. In *Organometallic Compounds in the Environment, Principles and Reactions* (ed. P J Craig), pp. 1-58. Harlow: Longman.

Lide D R (editor-in-chief) (1994) CRC Handbook of Chemistry and Physics (75th edn.). Boca Raton, FL: CRC Press.

Appendix D: Methodology for scoping calculations to estimate oxygen consumption and hydrogen production in unsaturated and saturated landfills

The redox conditions in a landfill containing metal residues will affect the gas generation processes. Hydrogen generation will be an important determinant of whether a landfill is anaerobic because:

- it is the bulk gas most likely to displace the initial inventory of air from the landfill;
- it will balance the slow ingress of air into the waste through the engineered barriers.

Preliminary calculations were performed to investigate the effect of metal corrosion on the evolution of the redox conditions of a landfill facility and the potential for hydrogen gas production. Calculation were performed for:

- an unsaturated landfill facility filled with waste and initially aerobic;
- a saturated landfill facility filled with waste and initially aerobic.

The results of the calculations are described in Section 6.

The methodology used and the assumptions required for each calculation are described below. In all cases, the calculations relate to the period after emplacement of the waste and capping of the landfill cell. No allowance is made for displacement of oxygen by any gases produced in the landfill.

Unsaturated landfill facility

Assumptions

- The landfill is initially aerobic and filled with waste.
- Oxygen ingress occurs only through the cap and the rate of ingress can be calculated from typical emission properties for a good permanent capping (10^{-3} mg $m^{-2}s^{-1}$) (A. Rosevear, personal communication).
- Oxygen transport through the waste voidage is rapid compared with transport through the cap and the mild steel corrosion rate.
- There is sufficient moisture present to maintain a film of water on corroding surfaces.
- The formation of corrosion products does not affect the rate of corrosion.
- All ferrous metal in the waste is assumed to be present as mild steel and appropriate corrosion rates can be applied.

- The aerobic corrosion rate for mild steel is assumed to be proportional to the partial pressure of oxygen present.
- The specific area of the mild steel in the waste can be represented by a single value that remains constant.
- The production of hydrogen gas does not impede the ingress of oxygen.

Methodology

For the above assumptions, the rate of change of oxygen concentration in the waste voidage is given by:

$$\frac{dc}{dt} = \frac{1}{p_{atm}V_{LF}}\left(K_1 p_{atm} - K_1 p - K_2 A_m p\right), \qquad \text{D1}$$

where:

c	is the gas phase oxygen concentration in the waste voidage;
t	is the time;
p	is the partial pressure of oxygen in the waste voidage;
p_{atm}	is the atmospheric partial pressure of oxygen;
V_{LF}	is the volume of the landfill voidage;
K_1	is the rate of oxygen ingress/egress expressed as the mass of oxygen entering the landfill per unit time (this rate is assumed to be proportional to the partial pressure of oxygen);
K_2	is the corrosion rate of mild steel under aerobic conditions expressed as the mass of oxygen consumed per unit area of corroding metal per unit time, at $p = p_{atm}$;
A_m	is the area of the corroding metal in the waste.

The steady-state partial pressure of oxygen (p_{ss}) is derived by assuming that the rate of change of oxygen concentration is zero, giving:

$$p_{ss} = \frac{K_1}{K_1 + K_2 A_m} p_{atm} . \qquad \text{D2}$$

When K_1 is much greater than K_2A_m, oxygen ingress dominates and the landfill remains aerobic. When K_1 is much less than K_2A_m, corrosion dominates, the partial pressure of oxygen tends to zero and the landfill becomes anaerobic. When K_1 and K_2A_m are comparable, the steady-state partial pressure of oxygen can be calculated from equation D2.

The value of K_1 has been derived from the second assumption above. The corrosion rate per unit area K_2 is given by:

$$K_2 = kz , \qquad \text{D3}$$

where:

k	is the corrosion rate expressed as the thickness corroded per unit time;
z	is the mass of oxygen consumed per unit volume of mild steel corroded.

An example of the values of the parameters used and the calculated rates and steady state partial pressure of oxygen are given in Table 6.1.

Calculation of timescale and hydrogen evolution profiles

For the case where K_1 is much less than K_2A_m, an estimation of the time for the landfill to be come anaerobic can be made for the assumption that oxygen ingress and egress can be neglected. Under these conditions equation D1 becomes

$$\frac{dc}{dt} = -\frac{K_2 A_m}{V_{LF}} \frac{p}{p_{atm}}, \qquad \text{D4}$$

or:

$$\frac{dc}{dt} = -\frac{K_2 A_m}{V_{LF}} \frac{c}{c_0}, \qquad \text{D5}$$

where:

> c_0 is the initial gas phase oxygen concentration in the waste voidage, corresponding to the atmospheric partial pressure of oxygen.

Integrating gives

$$c = c_0 \exp\left(-\frac{K_2 A_m}{V_{LF} c_0} t \right). \qquad \text{D6}$$

If it assumed that the landfill facility becomes anaerobic when the partial pressure of oxygen drops to 0.1 per cent of its initial value (i.e. $c/c_0 = 0.001$), then the time taken for anaerobic conditions to be achieved is given by:

$$t_{an} = -\log_e\left(\frac{1}{1000}\right)\frac{V_{LF} c_0}{K_2 A_m}. \qquad \text{D7}$$

Saturated landfill facility

Assumptions

- The landfill is saturated due to water ingress.
- Oxygen transport to corroding surfaces is limited by diffusion through water and is characterised by the free water oxygen diffusion coefficient. Oxygen transport by mixing due to convection or other process is assumed not to occur.
- The top layer of the landfill contains oxygen-saturated leachate at all times.
- Layers below the top layer contain oxygen-saturated leachate initially.
- Layers below the top layer contain corroding metal.
- The formation of corrosion products does not affect the rate of corrosion.
- All ferrous metal in the waste is assumed to be present as mild steel and appropriate corrosion rates can be applied.
- The rate of oxygen consumption by aerobic corrosion of mild steel is proportional to the oxygen concentration in the porewater.
- The specific area of the mild steel in the waste can be represented by a single value which remains constant.

Methodology

The concentration and time dependence of diffusion are characterised by Fick's Second Law. For diffusion in one dimension, this states:

$$\frac{dC}{dt} = D\frac{d^2C}{dx^2}, \qquad \text{D8}$$

where:

C is the aqueous concentration of the diffusing species;

x is the distance;

D is the free water oxygen diffusion coefficient.

Numerically the change in concentration at a given point and time can be calculated for a suitable time interval *Δt* and distance *L* corresponding to the thickness of the layer considered. The change in concentration at any time step and position is then given by:

$$\Delta C = \frac{D(C_{n-1} - C_n)}{L^2}\Delta t, \qquad \text{D9}$$

where:

C_{n-1} and C_n represent the aqueous concentrations in adjacent layers.

Similarly the change in concentration due to corrosion can be calculated for a given layer and time interval from:

$$\Delta C = \frac{kzA_m}{V_{LF}}\frac{C}{C_{sat}}\Delta t. \qquad \text{D10}$$

The parameters k, z, A_m, and V_{LF} are defined above in the methodology for an unsaturated landfill. The factor C/C_{sat} is required because the corrosion rate constant (k) is assumed to be measured under saturated aerobic conditions (i.e. $C = C_{sat}$). The implicit assumption is that the overall rate of corrosion is proportional to the oxygen concentration.

A spreadsheet calculation was set up using ten layers, with the boundary conditions defined in the second to fifth assumptions above. For each layer and time step, the reduction in concentration due to corrosion was calculated using equation D10. The new concentrations in each layer were then used to calculate the flux of oxygen between layers due to diffusion using equation D9. This process was repeated for a given number of time steps.

Verification of numerical procedure

The numerical methodology was verified for diffusion by comparison with an analytical solution to the diffusion equation. Corrosion was not represented (except that the concentration at a bounding surface was fixed at zero representing an idealised aerobically corroding surface that removes all oxygen that reaches it). The full boundary conditions were:

$C(x,0) = C_{sat}$,

$C(0,t) = 0$,

where:

$C(x,t)$ represent the aqueous concentration of oxygen at distance x and time t.

The analytical solution (de Marsily 1986) is given by:

$$C = C_{sat}\,\mathrm{erf}\left(\frac{x}{\sqrt{4Dt}}\right). \qquad \text{D11}$$

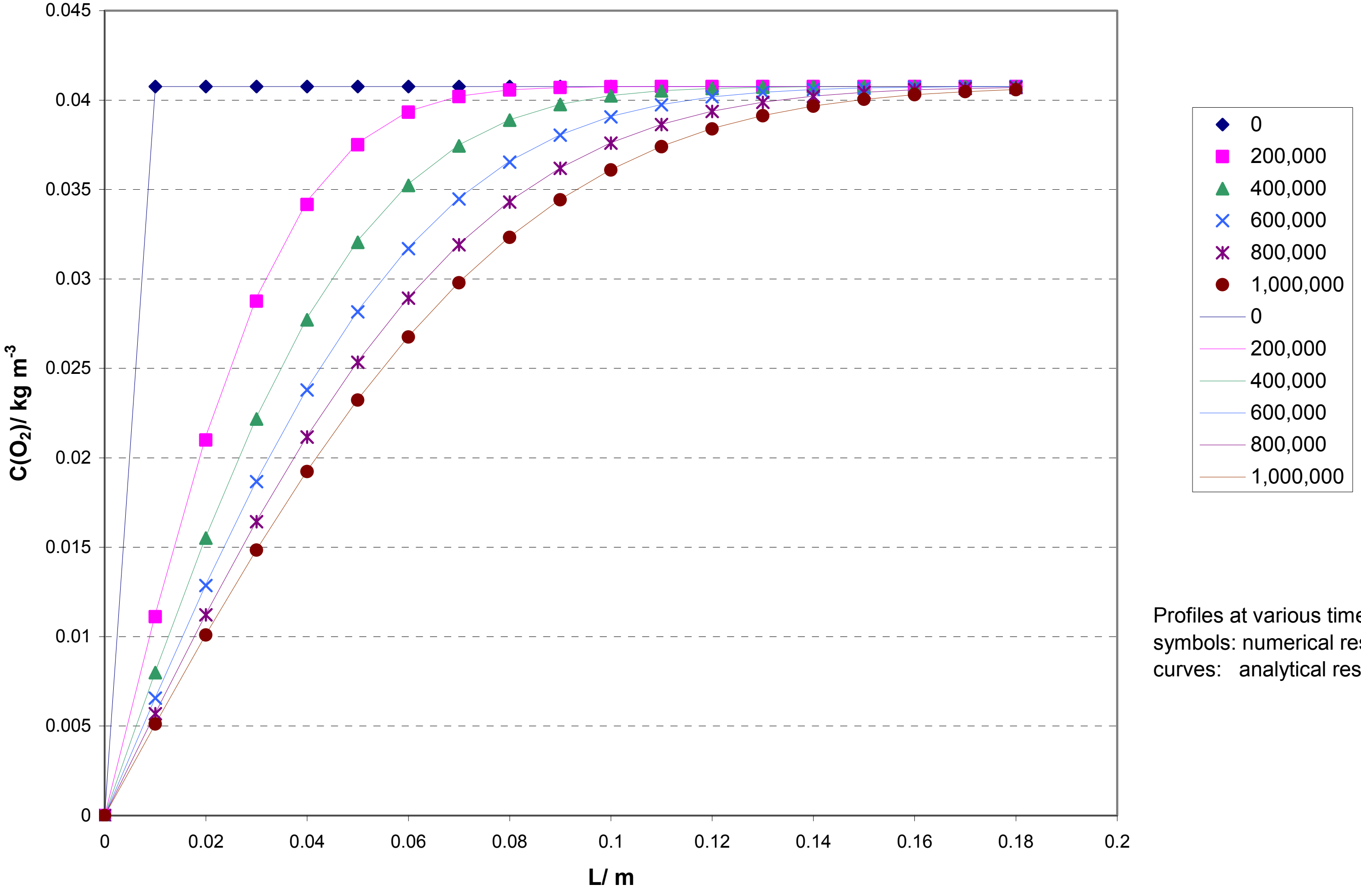
The numerical results gave very good agreement with the analytical solution as shown in Figure D1.

References

de Marsily G (1986) *Quantitative Hydrology: Groundwater Hydrogeology for Engineers.* London: Academic Press.

Figure D1 Depletion of oxygen as a function of time and distance – comparison of numerical and analytical results

D = 2 10^{-9} m^2s^{-1}, Boundary conditions: C =0 at L=0, C_{sat} = 0.0408 kg m^{-3} at t=0 and L>0



Profiles at various time/ seconds
symbols: numerical results
curves: analytical results

Appendix E: Detection of gaseous trace species likely to be present in inorganic landfill gas by gas indicator tube (Matheson Tri-Gas)

Table E1 lists species of possible interest that may be detected using tubes from one commercial source (Matheson Tri-Gas 2005), the measurement ranges and the potential interferences.

References

Matheson Tri-Gas (2005) *Detector tube listing for Matheson-Kitagawa toxic gas detector system*. Matheson Tri-Gas Technical Bulletin 102-1 Issue 3, downloaded as Model 8014 Kitagawa Tube List from Literature Centre/Speciality Gases & Equipment, http://www.matheson-trigas.com [Accessed August 2005].

Table E1 Gas indicator tube detection of gaseous trace species likely to be present in inorganic landfill gas[1]

Species	Typical concentration[2] in gas from existing landfills (or other experiments[3] ($g\ m^{-3}$)	Measuring range	Likely interferences
Group VIII			
$Ni(CO)_4$	(5×10^{-7} To 1×10^{-6})	20 ~ 700 ppm	Arsine, iron carbonyl, mercury vapour, H_2S or SO_2 (10), CO (1,000)
Group IIb			
Hg vapour	9×10^{-7} 1×10^{-8} to 1×10^{-5}	0.5 ~ 10, 0.1 ~ 2 mg m^{-3}	HCl(0.5), NO_2(0.1), Cl_2(0.1), H_2S (0.5)
Group IIIb			
Diborane		0.1 ~ 5, 0.05 ~ 2.5, 0.02 ~ 1 ppm	Arsine, phosphine, silane, disilane
Group IVb			
Simple hydrocarbons excluding methane (acetylene used as example)		50 ~ 1000 ppm	Olefins(10), H_2S(10), CO(50), NH_3, butadiene(25), HCN, Cl_2, NO_2, CS_2, benzene,
CO	6×10^{-3} (median)	25 ~ 1000, 5 ~ 300 ppm	Ethylene (5,000), H_2 (5,000), acetylene, SO_2 or NO_2 (at 0.2×CO)
		10 ~ 250 ppm	Acetylene(5), H_2S (20), SO_2 (0.2×CO), NO_2 (0.1×CO)
		20 ~ 1,000, 5 ~ 50 ppm	Ethylene or H_2 (5,000), acetylene (0.2×CO), SO_2 (0.2×CO), NO_2 (0.2×CO)
		1 ~ 50 ppm	SO_2, NO_2 or acetylene (0.02×CO), ethylene (1,000)
		0.1 ~ 2%	Propane (0.15%), *iso*-butane (0.2%), hexane (0.1%), acetylene (0.3%), ethylene (0.15%)
		30 ~ 500 ppm	Acetylene (0.05×CO), SO_2 (0.5×CO), NH_3 (100×CO), H_2S (0.5×CO)
		0.1 ~ 10%, 0.2 ~ 20%	Propane, *iso*-butane, acetylene, ethylene, hexane
COCl2	-	0.5 ~ 20, 0.1 ~ 0.5 ppm	Cl_2(5), HCl (10), NO_2(100) SO_2 (0.2%)
HCN	-	2 ~ 100, 0.5 ~ 25 ppm	SO2 (1), H2S (3), NH3 (5)
		0.01 ~ 3%	Acetone, CS_2, SO_2 (200), H_2S (100) Dicyanide
Silane	-	1 ~ 50, 0.5 ~ 25 ppm	PH_3 (20) arsine(50), disilane(2), diborane(20)

Table E1 (cont'd) Gas indicator tube detection of gaseous trace species likely to be present in inorganic landfill gas[1]

Species	Typical concentration[2] in gas from existing landfills (or other experiments[3] (g m^{-3})	Measuring range	Likely interferences
Group Vb			
NO_2	-	20 ~ 1000 ppm	Cl_2, Br_2, I_2 or ozone(5), NO (10)
		0.5 ~ 30 ppm	Cl_2, Br_2, or I_2 (2), NO (15)
		0.1 ~ 1 ppm	Ozone(2), SO_2(7), Cl_2(3)
Nitrogen oxides		20 ~ 250 ppm	SO_2(100), HCl(1000)
		100 ~ 2500 ppm	HCl(500)
		0.5 ~ 15, 15 ~ 30 ppm	H_2S(5), HCl(500)
NH_3	-	0.5 ~ 10%	Amines
		50 ~ 900 ppm	SO_2 (0.25×NH_3), Cl_2(2), amines
		10 ~ 260, 5 ~ 130 ppm	SO_2 (0.33×NH_3), Cl_2(2), amines
		1 ~ 20, 0.1 ~ 1 ppm	amines
		0.5 ~ 30%	H_2S (3,000)
		0.1 ~ 1%	Amines
Amines (for example of $N(CH_3)_3$	-	1 ~ 20 ppm	NH_3, other amines
PH_3	3×10^{-6} to 3×10^{-7}	20 ~ 700 ppm	Arsine(30), hydrogen selenide (50), H_2S (40)
		1~ 20, 0.5~ 10, 0.25 ~ 0.5 ppm	NH_3(60), arsine, H_2Se, nickel carbonyl
		0.1 ~ 0.2, 0.05 ~ 0.1 ppm	Hydrogen selenide, mercaptans, H_2S, HCN, SO_2, arsine
AsH_3	7×10^{-8}	5 ~ 160 ppm	H_2S (≥5 ppm), H_2Se (≥5 ppm), PH_3 (≥5 ppm)
		0.05 ~ 2ppm	H_2Se, mercaptans, H_2S, HCN, SO_2

Table E1 (cont'd) Gas indicator tube detection of gaseous trace species likely to be present in inorganic landfill gas[1]

Species	Typical concentration[2] in gas from existing landfills (or other experiments[3] (g m^{-3})	Measuring range	Likely interferences
Group VIb			
H_2S	3×10^{-2} to 6×10^{-1}*	6 ~ 300, 3 ~150, 1 ~ 50, 0.57 ~ 37.5 ppm	SO_2 (12), mercaptans (550), NO_2 (2)
		0.005 ~ 0.16%	CO (10), ethylene, propylene, butylene, acetylene or methyl mercaptan (5), HCN, NH_3
		1 ~ 30, 2 ~60 ppm	SO_2 (10), mercaptans (300), NO_2 (2)
		2 ~40, 1~ 20, 0.5 ~10 ppm	Phosphine, mercaptans, NH_3, NO_2
		50 ~ 1000, 100 ~ 2000 ppm	SO_2 (5,000), mercaptans
		0.1 ~ 4%	SO_2 (0.5%)
		0.05 ~ 0.6 0.1 ~ 1.2%	SO_2 (0.5%)
		0.2 ~ 3, 0.4 ~ 6 ppm	Arsine, hydrogen selenide, mercaptans, phosphine, HCN, SO_2
		2 ~ 20%	SO_2
		5 ~ 40%, 2.5 ~ 5%	SO_2 (8%)
SO_2	-	0.1 ~ 3%	H_2S (400)
		0.02 ~ 0.3%	H_2S (100)
		20 ~300 ppm	Cl_2 ($0.2\times SO_2$), NO_2 (100), H_2S ($100\times SO_2$)
		1 ~ 60 ppm	NO_2 ($1\times SO_2$), Cl_2 ($2\times SO_2$)
		0.5 ~ 10, 0.25 ~ 5 ppm	NO_2, HCl
		0.02 ~ 0.3%	H_2S (100)
H_2SO_4	-	0.5 ~ 5 mg m^{-3}	HCl, HF, NO_2, nitric acid, Cl_2

Table E1 (cont'd) Gas indicator tube detection of gaseous trace species likely to be present in inorganic landfill gas[1]

Species	Typical concentration[2] in gas from existing landfills (or other experiments[3] (g m^{-3})	Measuring range	Likely interferences
CS_2	1×10^{-3} to 2×10^{-1}*	2 ~ 50, 0.8 ~ 20 ppm	H_2S (120), SO_2, Cl_2
		30 ~ 500 ppm	H_2S (400), SO_2, Cl_2
COS	-	5 ~ 60 ppm	SO_2 (0.2×COS), CS_2 (0.1×COS), H_2S (0.5×COS), C_4H_9 (0.1%)
H_2Se	-	5 ~ 600, 1 ~100 ppm	Arsine (10), H_2S, iron carbonyl (10), SO_2, Hg, acetylene (3%), CO (0.1%), nickel carbonyl (10)
Group VIIb			
Hydrogen chloride	-	20 ~ 600, 40 ~1,200 ppm	SO_2, Cl_2
	-	4 ~ 40, 2 ~ 20, 0.4 ~ 4 ppm	Cl_2
Hydrogen fluoride	-	0.5 ~ 30, 0.25 ~ 15 ppm	Cl_2, HCl
Bromine	-	1 ~ 20 ppm	Cl_2 (1), ClO_2, NO_2
Chlorine	-	1 ~ 40 ppm	Br_2 (1), Cl_2O (1), NO_2 (0.5×Cl_2)
	-	0.5 ~10, 0.125~ 0.5, 0.1 ~ 0.5 ppm	Br_2 (1), Cl_2O (1), NO_2 (0.25×Cl_2), NCl_3(5)
	-	0.1 ~ 2, 0.05 ~ 1 ppm	HCl (20×Cl_2), NO_2
ClO_2	-	1 ~ 20 ppm	Br_2, Cl_2 or NO_2 (1)
CH_3I	-	5 ~ 40 ppm	H_2S (7), *n*-hexane (500), acetone (700), benzene (2), toluene (2), xylene (2), halogenated hydrocarbons

Notes:

[1] Matheson Tri-Gas (2005)

[2] Concentrations as the elements unless otherwise noted by * (* =concentration of molecular species)

[3] (Other experiments) denoted in brackets are for gas samples taken from above incubated sewage sludge or *M. formicicum* cultures in laboratory experiments** or gas sampled from sewage treatment plants***

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