# Aspects of Pretreated Hospital Waste Biodegradation in Landfills

Dem Fachbereich Ingenieurwissenschaften, Abteilung Maschinenbau der Universitaet Duisburg-Essen Zur Erlangung des akademischen Grades

# DOKTOR-INGENIEURIN

genehmigte Dissertation

Von

Qin Wang

aus Emei

Referent:: Prof. Dr. rer. nat. Jan-Dirk Herbell Korreferent:: Prof. Dr. Ing. Martin Faulstich Tag der muendlichen Pruefung: 2004-12-17

# Contents

1 Introduction	1
1.1 Definition of Health-care Waste ·····	• 1
1.2 The risks of Health-care Waste	• 3
1.3 Research Background ·····	••4
2 Fundamental Theory of Waste Landfilling	8
2.1 Biodegradation Process under Landfill Conditions	8
2.1.1 Aerobic Decomposition Process ······	• 8
2.1.2 Anaerobic Degradation Process ······	• 9
2.1.2.1 Hydrolysis Stage · · · · · · · · · · · · · · · · · · ·	•10
2.1.2.2 Acetogenisis Stage ······	•10
2.1.2.3 Methanogenisis Stage ·····	•11
2.2 Landfill Gas · · · · · · · · · · · · · · · · · · ·	• 16
2.2.1 Landfill Gas Components ·····	17
2.2.2 Landfill Gas Generation · · · · · · · · · · · · · · · · · · ·	17
2.3 Leachate ·····	18
2.3.1 Leachate Production ·····	19
2.3.2 Leachate Composition ·····	20
2.3.3 Factors Affecting Leachate Composition ·····	21
3 Materials and Methods	23
3.1 Introduction ·····	23
3.2 Experimental Setup ·····	•23
3.3 Waste Samples Preparation · · · · · · · · · · · · · · · · · · ·	•24
3.3.1 Municipal Solid Waste Samples ·····	•24
3.3.2 Sterilized Hospital Waste Samples ·····	•26
3.3.3 Hospital Waste Incineration Ash	•26
3.3.4 Mixture of Sterilized Hospital Waste and Municipal Solid Waste	·27
3.3.5 Mixture of Hospital Waste Incineration Ash and Municipal Solid Waste ······	•27
3.4 Analytical Methods · · · · · · · · · · · · · · · · · · ·	•27
4 Biodegradation of Sterilized Hospital Waste in Comparison with Municipa	Solid
Waste	33
4.1 Introduction · · · · · · · · · · · · · · · · · · ·	••33
4.2 Waste Characteristics of Sterilized Hospital Waste and Municipal Solid Waste ······	••••33
4.2.1 Comparison between Composition of Sterilized Hospital Waste and Municipal	
Solid Waste · · · · · · · · · · · · · · · · · · ·	•••33

4.2.2 Hydraulics of Landfill Reactors ····································	
4.2.3 Comparison between Biodegradable Carbon Content of Hospital Waste and Municipa	al
Solid Waste ····································	
4.2.4 Maximum Gas Prediction ····································	
4.3 Biodegradation Process of Sterilized Hospital Waste in Comparison with Municipal Solid	
Waste	
4.3.1 Gas Production of Sterilized Hospital Waste in Laboratory Test ••••••••••••••••••••••••••••••••	
4.3.2 Gas Composition ······40	
4.3.3 pH-value of Leachate ······42	
<b>4.3.4 COD of Leachate</b>	
4.3.5 Ammonium Concentration of the Leachate ····································	
4.3.6 Fatty Acids Concentration of the Leachate	
5 Co-disposal of Sterilized Hospital Waste with Municipal Solid Waste 48	
5.1 Introduction ······48	
5.2 Waste Characteristics of the Mixture of Sterilized Hospital Waste and Municipal	
Solid Waste · · · · · · · · · · · · · · · · · · ·	
5.2.1 Compostion of Sterilized Hospital Waste and Municipal Solid Waste $\cdots \cdots \cdots$	
5.2.2 Hydraulics of Landfill Reactors ······	
5.2.3 Biodegradable Carbon Content $\cdots \cdots \cdots$	
5.2.4 Maximum Gas Amount Prediction $\cdots \cdots \cdots$	
5.3 Co-disposal of Sterilized Hospital Waste with Municipal Solid Waste in Laboratory Test $\cdots$ 50	
5.3.1Gas Production $\cdots \cdots 50$	
5.3.2 Gas Composition $\cdots 52$	
5.3.3 pH-value of Leachate $\cdots \cdots \cdots$	
<b>5.3.4 COD of Leachate</b>	
5.3.5 Ammonium Concentration of Leachate ····································	
5.3.6 Fatty Acids Concentration of Leachate	
6 Leaching Behavior of Hospital Waste Incineration Ash and Co-disposal with	า
Municipal Solid Waste 58	
6.1 Introduction •••••••••58	
6.2 Leaching Behavior of Hospital Waste Incineration Ash $\cdots \cdots \cdots$	
6.2.1 Waste Characteristics and Hydraulics of Hospital Waste Incineration Ash	
Landfill Reactor $\cdots \cdots 58$	
6.2.2 Results and Discussion ······58	
6.3 Co-disposal of Hospital Waste Incineration Ash with Municipal Solid Waste $\cdots \cdots \cdots \cdots 62$	
6.3.1 Waste Sample Characteristics ····································	

6.3.2 Hydraulics ····································	
6.3.3 Biodegradable Carbon Content	
6.3.4 Maximum Gas Prediction ······62	
6.3.5 Results and Discussion ······63	
6.4 Discussion ······69	
7 Kinetic Model of Gas Production Rate 71	
7.1 Introduction · · · · · · · · · · · · · · · · · · ·	
<b>7.2</b> Model Selection · · · · · · · · · · · · · · · · · · ·	
<b>7.3 Model Derivation</b>	
<b>7.3.1 Rate Law of Reaction</b> ••••••••••••••••••••••••••••••••••••	
<b>7.3.2 Enzyme Reactions</b> • • • • • • • • • • • • • • • • • • •	
7.3.3 Kinetic Equation of Bacterial Growth · · · · · · · · · · · · · · · · · · ·	
7.3.4 Rate of Biogas Production ······74	
7.3.5 Model Determination ······75	
7.3.6 Model Simplification · · · · · · · · · · · · · · · · · · ·	
7.3.7 Mathematic Solution of the Kinetic Model · · · · · · · · · · · · · · · · · · ·	
7.3.8 Parameters Definition of the Kinetic Model · · · · · · · · · · · · · · · · · · ·	
7.4 Gas Production Rate Kinetic Model for Municipal Solid Waste with Leachate Recycling $\cdots$ 79	
<b>7.5 Discussion</b> ••••••83	
8 Diffusion Model for Biodegradation of Hospital Waste and Municipal	
Solid Waste 86	;
8.1 Introduction ······86	
<b>8.2 Fick's Law</b> •••••••86	
8.3 Differential Form of the Mass Diffusion Equation ••••••••••••••••••••••••••••••••••••	
8.4 Biodegradation Model · · · · · · · · · · · · · · · · · · ·	
8.4.1 Model Derivation · · · · · · · · · · · · · · · · · · ·	
8.4.2 Fatty Acids Accumulation Rate Model · · · · · · · · · · · · · · · · · · ·	
8.4.2.1 Modeling of Fatty Acids from Hydrolysis Stage ••••••••••••••••••••••90	
8.4.2.2 Rate of Fatty Acids Depletion ••••••••••••••••••••••••••••••••••••	
8.4.2.3 Fatty Acids Accumulation Rate Model · · · · · · · · · · · · · · · · · · ·	
8.4.3 Methanogenic Biomass Accumulation Model · · · · · · · · · · · · · · · · · · ·	
8.4.4 Complete Biodegradation Model · · · · · · · · · · · · · · · · · · ·	
8.5 Model Discussion · · · · · · · · · · · · · · · · · · ·	
<b>8.5.1Surface Area</b> · · · · · · · · · · · · · · · · · · ·	
8.5.2 Temperature · · · · · · · · · · · · · · · · · · ·	
8.5.3 Moisture Content $\cdots \cdots \cdots$	

8.5.4 Initial Organic Concentration	·····95
8.5.5 Fatty Acids Concentration · · · · · · · · · · · · · · · · · · ·	·····95
8.5.6 Initial Methanogenic Biomass Concentration · · · · · · · · · · · · · · · · · · ·	96
9 Conclusion and Outlook	97
References	101
Appendix	104

# Chapter 1 Introduction

Waste is always a sensitive topic for public, health-care waste is especially so. In public health-care waste is regarded as hazardous, perceiving a risk to both human health and the environment.

Since the nineteen fifties, health-care waste has been taken into focus in world wide area. In 1989, "Basel convention on the control of transboundary movements of hazardous wastes and their disposal" classified health-care waste as "hazardous waste". In 1998, China published a "national hazardous waste list", where infectious health-care waste is mentioned at the first position "HW01". Obviously, proper disposal and management of hospital waste is important for human health and environment.

This paper starts with definition of health-care waste and its disposal, subsequently concentrates on the fate of residues from two important treatment techniques – incineration and sterilization – and their effects on environment under landfill conditions. This paper explores into the reaction mechanism, and sets up a kinetic model of landfill gas production, and a model for biodegradation of organic compounds.

## **1.1 DEFINITION OF HEALTH-CARE WASTE**

Different countries have different definitions and classifications of health-care waste. The interpretation of the definition of health-care waste varies according to national circumstances, policies and regulations. International organizations – World Health Organization, the United Nations, etc. – have specific interpretations of the definition.

Based on Basel Convention, health care waste was defined as the solid or liquid wastes arising from medical activities such as diagnosis, monitoring, treatment, prevention of disease or alleviation of handicap in humans or animals, including related research, performed under the supervision of a medical practitioner or veterinary surgeon or another person authorized by virtue of his or her professional qualification. It includes a large component of non-risk waste and a smaller proportion of risk waste. Non-risk waste is similar to municipal waste and does not create more health or other hazards than mismanaged municipal waste. If the risk waste is not properly segregated from other waste fractions, the whole mixture has to be handled as infectious waste.

The risk waste is called hazardous health-care waste. It includes:

(a) Infectious health-care waste

All health-care waste known or clinically assessed by a medical practitioner or veterinary surgeon has the potential of transmitting infectious agents to humans or animals. It includes discarded materials or equipment contaminated with blood and its derivatives,

other body fluids or excreta from infected patients with hazardous communicable diseases, and laboratory waste.

- (b) Chemical, toxic or pharmaceutical waste, including cytotoxic drugs
- (c) Sharps
- (d) Radioactive waste
- (e) Other hazardous waste
- Fig. 1.1 shows the proportion of waste from clinics and hospitals.



Fig. 1.1: Waste from Clinics and Hospitals

In China, the "national hazardous waste list" defines health-care waste being clinically assessed waste from health care service of hospitals, medical treatment centers and clinics. It equals to the infectious health-care waste defined by Basel Convention. It includes: surgery residues and bands, biology and animal experiment residues, laboratory waste, infectious waste water and sludge, etc, listed as number one HW01. Chemical, toxic or pharmaceutical waste, cytotoxic drugs listed as number three HW03. Radioactive waste is listed as number sixteen HW16.

The standard of Ministry of Construction of China CJ/T3033-1996, "solid waste resource classification and generation", defined health-care waste as waste arising from hospital, epidemic prevention, sanatorium, veterinary surgeon, medical research and pharmacy, etc. It includes HW01, HW03 and HW16 in "national hazardous waste lists", and covers wider area.

On June 4 of 2003, the No. 380 regulation of Chinese State Council defined health-care

waste as infectious, toxic and hazardous waste arising from medical treatment, health-care, epidemic prevention, and related activities. It regulated the classification list of hospital waste to be defined by state sanitary ministry and state environmental protection agency.

#### **1.2 RISKS OF HEALTH CARE WASTE**

Health-care waste contains pathogens (including bacteria, viruses, rickettsia, parasites, fungi, hybrids and mutants) and sharps; exposure to health-care waste can induce disease or injury. The hazardous nature of health-care waste may be due to one or several of the following properties:

(a) It contains infectious agents.

The pathogenic micro-organisms may infect the human body through a crack or cut in the skin, or through the mucous membranes, and by inhalation and ingestion.

(b) It is cytotoxic or genotoxic.

The severity of health hazards for health-care workers handling cytotoxics arises from the combined effect of the substance toxicity and of the magnitude of exposure that may occur during waste handling or disposal. Exposure to cytotoxic substances in health care may also occur during preparation for treatment. The main pathways of exposure are inhalation of dust or aerosols, skin absorption, and ingestion of food accidentally in contact with cytotoxic drugs, chemicals or waste, or from contact with the secretions of chemotherapy patients.

(c) It contains toxic or hazardous chemicals or pharmaceuticals.

They may have toxic effects, either through acute or chronic exposure, and injuries, including burns. Intoxications can result from absorption of the chemicals/pharmaceuticals through the skin or the mucous membranes, and from inhalation or ingestion. Injuries can be provoked by contact of flammable, corrosive or reactive chemicals with the skin, the eyes or the mucous membrane of the lungs (e.g. formaldehyde and other volatile chemicals). The most common injuries are burns.

Mercury is another hazardous product common within hospitals owing to its prevalent use. It is most concentrated in diagnostic devices such as thermometers, blood pressure gauges and oesophageal dilators, Miller Abbott/Cantor tubes. It is also found in other sources such as fluorescent light tubes and batteries.

Disinfectants constitute a particularly important group of hazardous chemicals as they are used in large quantities, and are often corrosive. It should also be noted that reactive chemicals may form highly toxic secondary compounds. Chemical residues may be discharged into sewage treatment plants or to the natural ecosystems of receiving waters.

Pharmaceutical residues may have the same effects, as they may include antibiotics and other drugs, heavy metals such as mercury, phenols and derivatives and other disinfectants and antiseptics.

(d) It is radioactive.

Radioactive materials are unique in that they cause harm through both external radiation and through their intake into the body. Exposure to radiation from high-activity sources, such as those used in radiotherapy, can cause severe injuries, ranging from superficial burns to early fatalities.

(e) It contains sharps.

Sharps may not only cause cuts and punctures but also infect the wounds by agents which previously contaminated the sharps.

# **1.3 RESEARCH BACKGROUND**

Health-care waste poses serious risks to the environment. It is obviously important to find a suitable way to treat hospital waste with respect to the health impacts.

The problem of healthcare waste disposal is essentially biological: we wish to minimize the risk of disease causing bacteria and viruses moving from the hospital or research institution into the community. Pathogen destruction is the main task of healthcare waste disposal. Among all specific technologies to treat healthcare waste, two important techniques – incineration and sterilization – become focus topics on this specific field.

At first sight, incineration of healthcare waste might appear to be a reasonable solution. The reason for this is simple: incineration is certainly capable of destroying the bacteria and viruses. For this reason, incineration becomes the main technique to treat with healthcare waste in many countries including China. However, incineration of healthcare waste changes the biological problem into chemical problems. While destroying bacteria and viruses, incineration forces on itself the extra task of having to destroy the material on which the pathogens are sitting. Due to the high content of plastics in healthcare waste, acid gases are generated from the chlorinated organic plastics, dioxins and furans are formed from any chlorine present in the waste. In 1987, Hagenmaier<sup>[1]</sup> and co-workers in Germany reported that the levels of dioxins and furans in the fly ash collected from medical waste incinerators could be two orders of magnitude higher than the levels found in the fly ash in municipal waste incinerators.

Table 1.1 lists the data presented by Hagenmaier et al.

Constituent	Municipal solid waste incinerator	Hospital waste incinerator
	(ng/g)	(ng/g)
2,3,7,8-TCDD	0.03-0.34	1.4-3.4
Tetra CDD	0.6-7.5	94-404
Penta CDD	1.2-13.2	208-487
Hexa CDD	1.4-15.8	271-411
Hepta CDD	1.8-25.6	189-307
Octa CDD	1.9-23.1	123-245
Total dioxins	6.9-80.3	1155-1737
Tetra CDF	9.0-32.1	199-376
Penta CDF	10.2-38.3	285-647
Hexa CDF	8.0-31.7	253-724
Hepta CDF	3.4-15.9	125-286
Octa CDF	0.7-4.6	25-134
Total furans	31.3-119.5	895-2140

Table 1.1: Concentrations of Dioxins and Furans in Fly Ash from Municipal and Hospital Waste Incinerators

Moreover, medical waste incinerators were fitted with less advanced air pollution control because of high cost, and less professionally trained staff than municipal waste incinerators.

The cost of flue gas pollution control equipment of incinerators is very high. In Holland about half the capital cost of building new municipal waste incinerators is going into the flue gas pollution control equipment. For example, the 2000 tons/day incinerator in Amsterdam cost approximately \$600 million, with about \$300 million spent on flue gas pollution control equipment. To be able to recover the financial investment it is necessary to build these facilities larger and larger. However, the hospital waste incinerator is very small in comparison with municipal solid waste incinerators. In the U.S. the smallest hospital waste incinerators burn less than one ton per day, and the largest burn 50 to 100 tons per day. For such small incinerators, the proportion of capital cost for high level flue gas pollution control is too large. It usually involves swallowing the capital cost.

Health experts and community groups have opposed medical waste incineration. Many countries are looking for viable cleaner and safer and cheaper alternatives to incineration of medical waste. Non-incineration medical waste treatment technologies should provide the same level of pathogen destruction as incineration without negative environmental issues,

essentially solve this biological problem instead of changing to chemical problems. Leaded by suitable separated sorting and followed by correct recycling and landfilling, appropriate non-incineration medical waste treatment can solve this essential biological problem in a biological way. Among non-incineration medical waste treatment technologies, sterilization is paid a lot of attention on for the advantages as clean, safe, cheap and odourless. As a non-burning treatment technology, sterilization process does not create harmful emissions and needs much lower costs in operation and construction.

There are a lot of arguments on incineration and non-incineration medical waste treatment technologies. However, there is still lack of concrete data on which technique might be better for environment and human health. If economical aspects of techniques are decided by financial feasibility, public will naturally ask what the environmental impacts of these two technologies are. Are the residues after incineration or sterilization still hazardous to the environment? How to finally settle down the medical waste treatment residues? Up to now, no research work was done on this specific field. Therefore, this investigation focuses on the fate of the residues after incineration and sterilization treatment. The research focuses not only on the long-term leaching behavior of medical waste incineration ash and sterilized medical waste, but also on their effects on the biodegradation process when they were sent to a municipal solid waste landfill site. The potential effect of medical waste incineration ash and sterilized medical waste on a landfill site is investigated. The research results will provide concrete data for the foundation of an optimal hospital waste management system.

Incineration ash of medical waste was thought to be hazardous because of the problems of heavy metals and dioxins. A lot of research work was done on the leaching test of pure incineration ash. However, no research work was done on the effects of incineration ash on a municipal solid waste landfill site. No concrete data is available to show whether it is advantageous or dangerous for the biodegradation process under landfill conditions. This research tested not only the pure hospital waste incineration ash's leaching behaviour under landfill conditions, but also the reaction of a mixture of hospital waste incineration ash and municipal solid waste. In the same way the final fate of sterilized hospital waste is investigated. With the research results, proper treatment of medical waste incineration ash will be concluded.

Fig.1.2 illustrates the focus of this thesis. "Hospital waste (HSW)" is used to summarize all kinds of wastes mentioned before like "health-care waste" and "medical waste".



Fig. 1.2: Focus of this Thesis

# **Chapter 2 Fundamental Theory of Waste Landfilling**

During the earlier decades, landfilling of waste has developed to a great extent. Much information and experience in landfill design and operation has been obtained. Today in some industrialized countries, like Germany, incineration is the prevailing system for waste disposal, while landfilling still plays a most important role in many countries, and will remain an integral part of solid waste management. It is important to point out that not necessarily does landfill in different countries mean sanitary landfill. In developing countries, and even in well developed countries, open dumps or poorly managed landfills exist. Secondly, we must consider that even in those countries with low landfill utilization, landfill still plays the important role of receiving ashes and slag from combustion processes. Even in the case of Germany, biological treatment of organic waste, either aerobic biodegradation or fermentation, which in principle is the same as organic biodegradation under landfill conditions, is one of the heated topics of waste. Landfill is especially suitable to treat the low heat value waste containing high content of water and organics like in China.

In this chapter, the reaction mechanism of biological treatment of solid waste will be discussed together with the effect factors, as well as the landfill gas quality and utilization, leachate composition and treatment.

# 2.1 BIODEGRADATION PROCESS UNDER LANDFILL CONDITIONS

The environmental impacts of landfilling are today well recognized, and at most sanitary landfills measures are taken to control them. The degradation processes inside the landfill are the key to understanding and controlling the environmental impacts. Physical, chemical and biological processes are taking place in the waste and result in the release of gaseous and dissolved compounds in terms of landfill gas and leachate. In most landfills, assuming that they receive some organic wastes, the microbial processes will dominate the stabilization of the waste and hence govern the generation of landfill gas and the composition of leachate.

This chapter briefly describes the basic biochemical processes taking place in a landfill in terms of the active microbial consortium undertaking the degradation, and of the abiotic factors such as oxygen, hydrogen, pH and alkalinity, sulphate, nutrients, inhibitors, temperature and moisture/water content.

#### 2.1.1 Aerobic Decomposition Process

During the initial placement of refuse and at the surface of the landfill, aerobic

decomposition occurs. The reaction for aerobic digestion may be represented by following equation:

$$C_a H_b O_c N + O_2 \rightarrow CO_2 + H_2 O + NH_3$$
(2.1)

Oxygen will always diffuse from the atmosphere into the landfill waste. However, aerobic bacteria in the top layers of the landfill waste will readily consume the oxygen and limit the aerobic zone to less than 1 m of compacted waste. Extensive gas recovery pumping may create a substantial vacuum in the landfill, forcing atmosphere air to enter the landfill. This may extend the aerobic zone and eventually prevent formation of methane in these layers.

# 2.1.2 Anaerobic Degradation Process

The predominant part of the landfill waste will soon after disposal become anaerobic. The anaerobic degradation can be viewed as consisting of different stages. In this thesis, a three stages model is used, it consists of: hydrolysis, acetogenesis and methanogenesis. Fig. 2.1 illustrates the most important biochemical reactions involved in decomposition in a landfill.



Fig. 2.1: Simplified Biochemical Pathways<sup>[28]</sup>

#### 2.1.2.1 Hydrolysis Stage

The first stage is hydrolysis. During hydrolysis, complex polymeric organic compounds break down to monomeric compounds like sugars/alcohols, amino acids and fatty acids, hydrogen, carbon dioxide.

The hydrolysis process is a very important process in the landfill environment since the present solid organic waste must be solubilized before the microorganisms can convert it. After the smaller, easily soluble part of the organic matter has been converted, the hydrolysis may prove to be the overall rate-limiting process in the landfill environment. The hydrolysis is caused by extracellular enzymes produced by the fermenting bacteria.

Examples of chemical reactions during this process are shown in the following:

$$C_{6}H_{12}O_{6} + 2H_{2}O \rightarrow 2CH_{3}COOH + 4H_{2} + 2CO_{2}$$

$$C_{6}H_{12}O_{6} \rightarrow CH_{3}C_{2}H_{4}COOH + 2H_{2} + 2CO_{2}$$

$$C_{6}H_{12}O_{6} \rightarrow 2CH_{3}CH_{2}OH + 2CO_{2}$$
(2.2)

Following a series of experiments on the digestion of insoluble cellulose, Lee and Fan <sup>[3,4]</sup> (1982,1983) concluded that the kinetics of enzymatic hydrolysis are controlled by the structure of the cellulose substrate and the interaction activity between enzyme and substrate. Since the main degradable constituent of waste refuse is cellulose, their findings provide a useful starting point for a functional description of hydrolysis in waste refuse. Lee and Fan suggested that the rate limiting influence on enzymatic hydrolysis caused by changes in substrate structure or morphology resulted from a combination of surface area effects and changes in crystallinity.

Lee and Fan proposed another limiting factor to reflect reductions in enzyme-substrate activity due to product inhibition.

Hydrolysis of solid waste is a surface phenomenon occurring at the interface between the aqueous and solid phases, moisture has a distinct influence on the hydrolysis process of solid waste. It is not simply the presence of moisture that influences hydrolysis process, the moisture regime and the movement of moisture provides a vector by which microbially mediated processes can penetrate the waste mass. Reduction in moisture content may not affect hydrolysis rates by simply reducing the bulk phase volume in which reactions occur, in fact over certain ranges, reductions in moisture contents may influence enzymatic hydrolysis by interfering with the mobility of free enzymes and products.

#### 2.1.2.2 Acetogenis Stage

In the acetogenic stage, an acetogenic group of bacteria converts the products from the first stage to acetic acid. The acetogenic bacteria produce acetic acid, hydrogen and also

carbon dioxide if the volatile fatty acid being converted contains an odd number of carbon atoms, while aromatic hydrocarbons (e.g. benzene and toluene) apparently are not degraded.

Some of the important chemical reactions during acetogenic process are shown in the following.

$$CH_{3}CH_{2}COOH + 2H_{2}O \rightarrow CH_{3}COOH + CO_{2} + 3H_{2}$$

$$CH_{3}C_{2}H_{4}COOH + 2H_{2}O \rightarrow 2CH_{3}COOH + 2H_{2}$$

$$CH_{3}CH_{2}OH + H_{2}O \rightarrow CH_{3}COOH + 2H_{2}$$

$$C_{6}H_{5}COOH + 4H_{2}O \rightarrow 3CH_{3}COOH + H_{2}$$
(2.3)

The bacteria responsible for acid fermentation are relatively tolerant to changes in pH and temperature and have a much higher rate of growth than the bacteria responsible for methane fermentation. As a result, methane fermentation is generally assumed to be the rate-controlling step in anaerobic waste treatment processes.

#### 2.1.2.3 Methanogenisis Stage

In the methanogenisis stage, methane is produced by the methanogenic bacteria. The methanogenic bacteria are obligated anaerobic and require very low redox potentials. One group, the hydrogenophilic, converts hydrogen and carbon dioxide to methane, while another group, the acetogenic, converts primarily acetic acid to methane and carbon dioxide. The methanogenic bacteria may also convert formic acid and methanol. Some of the important reactions are shown in the following.

$$4H_{2} + CO_{2} \rightarrow CH_{4} + 2H_{2}O$$

$$CH_{3}COOH \rightarrow CH_{4} + CO_{2}$$

$$HCOOH + 3H_{2} \rightarrow CH_{4} + 2H_{2}O$$

$$CH_{3}OH + H_{2} \rightarrow CH_{4} + H_{2}O$$
(2.4)

The conversion of acetic acid to methane is by far the most important part of the methane-forming process.

The organic fraction of the waste making up the substrate for the microbial consortium is of highly varying nature, ranging from easily degradable organics such as food wastes, to hardly degradable organics such as lignin and polymers. The degradability of the waste highly affects the degradation rates.

The major abiotic factors affecting the methane formation in the landfill are discussed below.

# pH and alkalinity

The methane bacteria are quite sensitive to changes in pH. It has been found <sup>[5]</sup> that the

rate of methane fermentation is relatively constant within the pH range of 6 to 8, but drops very rapidly outside this range.

Fig. 2.2 shows the relative methane production rate as a function of pH for a mixed culture of methanogens.

Relative methane production rate



Fig. 2.2: Effects of pH on the Rate of Methane Fermentation

The methanogenic ecosystem in the landfill is rather delicate, and balanced relations between the various bacteria groups are crucial for a good methane production rate. Sufficient alkalinity is essential for proper pH control in anaerobic treatment because it acts as a buffer to the system. The presence of buffering material in the landfill (e.g. demolition waste, soil) will significantly improve the ability of the landfill environment to maintain a reasonable pH range.

#### **Cation concentration**

It has been found <sup>[5]</sup> that the rate of methane formation is affected by cation concentration. Obviously this effect comes from the nutrient function of the cations, as described by Haldane Equation. Such an effect is illustrated in Fig. 2.3, which shows that over a range of relatively low concentrations, cations have a stimulatory effect on the system. However, an optimum concentration exists which, when exceeded, will result in a decrease in the rate of methane fermentation. The degree to which the reaction is retarded at high cation

concentrations depends on the extent to which the optimum concentration is exceeded. The relative effects of some common cations on the rate of methane fermentation are given in Table 1.



Fig. 2.3: Effects of Cations on Methane Fermentation

Cation	Stimulatory	Moderately inhibitory	Strongly inhibitory
	concentration	concentration	concentration
	(mg/l)	(mg/l)	(mg/l)
Calcium	100-200	2500-4500	8000
Magnesium	75-150	1000-1500	3000
Potassium	200-400	2500-4500	12000
Sodium	100-200	3500-5500	8000

Table 2.1: Effects of Cations on Methane Fermentation

# Temperature

Like all other microbic processes, the anaerobic waste degradation rate is highly affected by temperature. Temperature can exert an effect upon biological systems in two ways: by influencing the rates of enzymatically catalyzed reactions and by affecting the rate of diffusion of substrate to the cell. The methanogenic bacteria contain a mesophilic group with a rate maximum around  $40^{\circ}$ C, and a thermophilic group with a maximum around  $70^{\circ}$ C. Only the former group is relevant in landfills. In laboratory simulations of landfill processes, the methane production rate has been proven to increase significantly (up to 100 times), when the temperature is raised from  $20^{\circ}$ C to 30 and  $40^{\circ}$ C. Landfill temperatures of  $30-45^{\circ}$ C should be possible even in temperate climates.

#### **Nutrients**

The anaerobic ecosystem must, besides organic matters, have access to all required nutrients, in particular nitrogen and phosphorous. All the necessary micronutrients, e.g. sulphur, calcium, magnesium, potassium, iron, zinc, copper, cobalt, molybdanate and selenium, are considered to be present in most waste landfills. The anaerobic ecosystem assimilates only a very small part of the substrate into new cells and therefore requires much less nitrogen and phosphorous than the aerobic system. Optimal ratios between organic matter (expressed as chemical oxygen demand), nitrogen and phosphorous are listed as 100:0.44:0.08<sup>[6]</sup>. On average, the mixed waste landfill will not be limited by nitrogen and phosphorous, but insufficient homogenization of the waste may result in nutrient-limited environments. Phosphorus is, if any, the nutrient most likely limiting the anaerobic degradation process.

#### Inhibitors

The methane-forming ecosystem is considered to be rather sensitive to inhibitors.

The absence of oxygen is a must for the anaerobic bacteria to grow and perform the above-mentioned processes. The methanogenic bacteria are the most sensitive to oxygen, they require a redox potential below -330mV.

Hydrogen is produced by both the fermentative and the acetogenic bacteria, and the generated hydrogen pressure affects the biochemical pathways. The fermentative bacteria yield hydrogen, carbon dioxide and acetic acid at low hydrogen pressures, while hydrogen, carbon dioxide and ethanol, butyric acid and propionic acid are generated at higher hydrogen pressures. The last three organic compounds may be further converted by the acetogenic bacteria, if the hydrogen pressure is not too high. The conversion of propionic acid requires hydrogen pressures below  $9 \times 10^{-5}$  atmospheres. This shows that if the hydrogen pressure is high, propionic and butyric acid will be generated, but not further converted.

Hydrogen is being consumed by the methanogenic and sulphate-reducing bacteria. Even at hydrogren pressures below 10<sup>-5</sup> atmospheres formation of methane from hydrogen and

carbon dioxide is favourable. If the hydrogen-consuming bacteria, due to other factors, decrease their activities, low hydrogen pressures cannot be sustained in the landfill and the above mentioned accumulation of volatile fatty acids, in particular propionic acid, will take place.

Sulphate is a major compound of many waste types (demolition waste, incinerator slag, fly ashes). The sulphate-reducing bacteria are obligate anaerobic and may convert hydrogen, acetic acid and higher volatile fatty acids during sulphate reduction. However, the organic carbon is always oxidized to carbon dioxide as opposed to the conversion by the methanogenic group of bacteria. A high activity of sulphate reducers hence may decrease the amount of organics available for methane production. Some of the sulphate reducing reactions are shown in the following.

$$4H_{2} + SO_{4}^{2-} + H^{+} \rightarrow HS^{-} + 4H_{2}O$$

$$CH_{3}COOH + SO_{4}^{2-} \rightarrow CO_{2} + HS^{-} + HCO_{3}^{-} + H_{2}O$$

$$2CH_{3}C_{2}H_{4}COOH + SO_{4}^{2-} + H^{+} \rightarrow 4CH_{3}COOH + HS^{-}$$
(2.5)

Several experiments <sup>[7,8]</sup>, both batch experiments and laboratory landfill simulators, have shown that when sulphate is present, the methane production is dramatically reduced. Increase in methane production and decrease in sulphate concentration is simultaneous. The suppression of methane formation by sulphate is not related to any toxic effects of sulphate on methanogenic bacteria but due to simple substrate competition. For pure cultures of methanogenic bacteria sulphate does not suppress methane formation but, if a sulphate-reducing strain is present, suppression is substantial due to the higher energy vielded by sulphate reduction. In addition, H<sub>2</sub>S may be toxic for methanogenic bacteria. So the pH should not be too acid, e.g. at pH > 7, more than 50% of H<sub>2</sub>S is not toxic any more. The inhibitory effects of volatile fatty acids have been investigated in several cases <sup>[9-11]</sup>. Inhibitory effects were not observed by Kugelman and Chin at total concentrations of acetic acid, propionic acid and butyric up to 6000 mg/L. Pure cultures have proven even less sensitive to substrate concentrations. In landfill environments, volatile acid concentrations will rarely reach levels where inhibitory effects on methane production will be expected. Several laboratory investigations <sup>[12,13]</sup> have shown that the methane production rate increases for increasing moisture content of the waste. Findings from the literature suggest an exponential increase in gas production rates between 25 and 60% water content. Specific environmental factors considered to be optimum for methane fermentation are presented in Table 2.2.

Variable	Optimum	Extreme
Temperature (°C)	30-35	25-40
рН	6.8-7.4	6.2-7.8
Oxidation-reduction potential MV	-520 to -530	-490 to -550
Volatile Acids (mg/l as acetic)	50-500	2000
Alkalinity (mg/l as $CaCO_3$ )	2000-3000	1000-5000

$a_{1}a_{2}a_{2}a_{3}a_{3}a_{3}a_{3}a_{3}a_{3}a_{3}a_{3$
--

# 2.2 LANDFILL GAS

Gas generated in the landfill (LFG) is a result of a mass transfer process. The main components of the landfill gas (CH<sub>4</sub>, CO<sub>2</sub>) are a result of biological processes, while the trace components, which are numerous, are generated by biological processes as well as by volatilization.

Migration of gas into the surrounding areas was observed in terms of dying trees and mal-growth of crops on agricultural fields. Explosions occurred, where gas accumulated in buildings and manholes in or adjacent to the landfills, and was ignited by the use of open fires or electrical sparks.

Landfill gas control started in the late 1960s and early 1970s in the USA. Gas utilization can be direct thermal utilization (e.g. in industry) and electricity production using gas engines. It may also be upgraded to natural gas quality by removing CO<sub>2</sub>. However, there are a great number of organic trace components in LFG that are responsible for severe corrosion problems in the gas pretreatment plants and in gas engines. Since about 120-150m<sup>3</sup> of LFG/t dry MSW with a calorific value of 5.9 kWh/m<sup>3</sup> (energy value about two-thirds that of natural gas) are produced <sup>[14]</sup>, there is a great energy potential available. LFG utilization had been seen as a big business in the early days in USA while this has changed with time. In Germany the main emphasis for LFG utilization was also commercial until it was realized that no big profits could be made. The economics of LFG are of course closely linked to energy prices.

The reasons for LFG abstraction and utilization changed. While in some states in USA gas abstraction was done to control releases of carcinogenic trace component vinyl chloride, explosion control and vegetation protection became more and more relevant in other countries. Today also the contribution of LFG emissions to the greenhouse effect is a reason in many countries that LFG extraction and utilization plants are mandatory at all new landfills.

# 2.2.1 Landfill gas components

The main components of landfill gas over relatively short times after disposal are 55% methane and 45% carbon dioxide. These concentrations remain relatively constant. A change of LFG composition inside the landfill will take place when oxygen enters the landfill. This has been observed only during gas extraction when air has been sucked into the landfill.

Besides the main components, the landfill gas also contains a certain amount of trace components. The type and concentration of these trace components depends on the composition of the landfilled wastes.

H<sub>2</sub> may also be found in full-scale landfills, but only over short periods of time.

O<sub>2</sub> appears in the gas only in the early phase of gas generation.

Sulphur components are mainly responsible for the odour of the gas. Some of these components, like hydrogen sulphide and the mercaptans, belong to the more toxic landfill gas components.

Hydrocarbons may be naturally generated in the landfill as well as deposited with the landfilled waste.



# 2.2.2 Landfill gas generation

Fig. 2.4: Development of Landfill Gas Composition<sup>[14]</sup>

Fig. 2.4 illustrates such an idealized sequence of landfill gas generation for a homogeneous volume of waste. It involves five distinct phases.

Phase 1, this is a short aerobic phase immediately after landfilling the waste, where easily degradable organic matter is aerobically decomposed during carbon dioxide generation. This stage, due to the exothermicity of reactions of biological oxidation, may reach elevated temperatures.

Phase 2, a first intermedial anaerobic phase develops immediately after the aerobic phase. The activity of the fermentative and also the acetogenic bacteria results in a rapid generation of volatile fatty acids, carbon dioxide and some hydrogen.

Phase 3, a second intermedial anaerobic phase will start with slow growth of methanogenic bacteria. The methane concentration in the gas increases, while hydrogen, carbon dioxide and volatile fatty acid concentrations decrease.

Phase 4, the methane phase is characterized by a fairly stable methane production rate resulting in a methane concentration in the gas of 50%-65% by volume. The high rate of methane formation maintains.

Phase 5, only the more refractory organic carbon remains in the landfilled waste. The methane production rate is low, nitrogen and oxygen start appearing in the landfill gas again due to diffusion from the atmosphere.

#### 2.3 LEACHATE

The major environmental impact associated with landfills is related to discharge of leachate into the environment, and the current landfill technology is primarily determined by the need to prevent and control leachate problems.

To prevent groundwater pollution, first step in landfill design was to site the landfill far from the groundwater. A further step was to site the landfill in a low permeability soil or to engineer impermeable liners to contain wastes and leachate. Leachate control strategies involve the input (waste and water), the landfill reactor and the output (leachate and gas).

Waste input control includes reducing to a minimum the amount of waste to be landfilled. This could be obtained by separate collection, recycling, incineration and composting. Another step is to reduce waste to a non-leachability level. This could be achieved by incineration followed by fixation of the solid residues. Pretreatment could also aim to reduce the biodegradability of waste to be landfilled. This would reduce or even eliminate the need for process water in the biostabilization. One way of reaching this aim is to pretreat waste by mechanically sorting organic matter and paper. This material could then be either composted or anaerobically digested.

The strategy for water input control is strictly related to the quality of waste to be landfilled.

In the case of non-biodegradable waste, prevention of water infiltration can be adopted as the main option (normally by means of top sealing). On the contrary, in the case of biodegradable waste, a water input must be assured until a reasonable degree of biostabilization is achieved. In this case the water input should be limited to the strictly necessary amount, and minimization techniques should be applied.

The main option in controlling leachate quality through controlling the landfill reactor is the enhancement of the biochemical processes when biodegradable wastes are deposited. One of the main objectives is to convert and transport as much carbon as possible from the solid phase into the gas phase rather than into the liquid phase. This is achieved by acceleration of the methane generation step.

Leachate discharge is the parameter traditionally controlled. One of the methods adopted is lining. A rational drainage and collection system is important to avoid emission or accumulation of leachate inside the landfill. According to increasingly restrictive limits for wastewater discharge, complicated and costly treatment facilities for leachate are imposed. The aspects of leachate production and composition (including water balances, characterization methods and factors controlling composition), as well as affecting factors for leachate composition, are described in the following.

#### 2.3.1 Leachate Production

Determination of the amount of water infiltrating a covered landfill cell can be made from the hydrological balance of the top cover, paying attention to precipitation, surface run-off, evapotranspiration, and changes in moisture content of the soil cover. The water content of the waste being landfilled is usually below saturation (actually field capacity) and will result in absorption of infiltrating water before drainage in terms of leachate is generated. Besides, improvement of top covers to store moisture for the dry season, establishing short-rotation tree plantations on landfill sections, and irrigation with leachate may also prove – even in relatively cold climates – an effective means of reducing the leachate generation rate. For a given area of landfill, prediction of the volume of leachate can be represented by the

(2.6)

Where L = leachate production

following simplified equation:

P = precipitation

R = surface run-off

 $riangle U_s$  = change in soil moisture storage

ET = actual evaporative losses from the bare soil/vegetated surface

 $\triangle U_w$  = change in moisture content of the refuse components

#### 2.3.2 Leachate Composition

Leachate composition has been the object of numerous research studies <sup>[15]</sup> because leachate treatment and disposal has been and still remains one of the main problems in sanitary landfill management.

The leachate composition in different phases of degradation is described in the following:

- Aerobic degradation phase. Usually the aerobic phase is short and no substantial leachate generation will take place.
- Acid-fermentation phase. It causes a decrease in leachate pH, high concentration of volatile acids and considerable concentrations of inorganic ions. The initial high content of sulphates may slowly be reduced as the redox potential drops. The generated sulphides may precipitate iron, manganese and other heavy metals that were dissolved by the acid-fermentation. The decrease in pH is caused by the high production of volatile fatty acids and the high partial pressure of CO<sub>2</sub>. The increased concentration of anions and cations is due to lixiviation of easily soluble material including that originally available in the waste mass and that made available by degradation of organic substances. Leachate from this phase is characterized by high BOD<sub>5</sub> values (commonly >10000mg/l), high BOD<sub>5</sub>/COD ratios (commonly >0.7) and acidic pH values (typically 5-6) and ammonia (often 500-1000mg/l), the latter due to hydrolysis and fermentation of proteinous compounds in particular.
- Intermediate anaerobic phase starts with slow growth of methanogenic bacteria. This growth may be inhibited by an excess of organic volatile acids which are toxic to methanogenic bacteria at concentrations of 6000-16000mg/l. The methane concentration in the gas increases, whilst hydrogen, carbon dioxide and volatile fatty acids decrease. Moreover, the concentration of sulphate decreases owing to biological reduction. Conversion of fatty acids causes an increase in pH values and alkalinity with a consequent decrease in solubility of calcium, iron, manganese and heavy metals. The latter are probably precipitated as sulphides. Ammonia is released and is not converted by an anaerobic environment.
- Methanogenic fermentation phase. The pH range tolerated by methanogenic bacteria is extremely limited and ranges from 6 to 8. At this stage, the composition of leachate is characterized by almost neutral pH values, low concentrations of volatile acids and total dissolved solids, whilst biogas presents a methane content which is generally higher than 50%. This confirms that solubilization of the majority of organic components has decreased at this stage of landfill operation, although the process of waste stabilization will continue for several years. Leachate produced during this stage

is characterized by relatively low BOD value and low ratio of BOD/COD. Ammonia continues to be released by the stage acetogenic process.

Fig. 2.5 illustrates the leachate composition development in landfills



VFA: Volatile Fatty Acids

Fig. 2.5: Leachate Composition Development in Different Phases <sup>[15]</sup>

# 2.3.3 Factors Affecting Leachate Composition

Waste composition: The nature of the waste organic fraction influences considerably

the degradation of waste in the landfill and thus also the quality of the leachate produced. The inorganic content of the leachate depends on the contact between waste and leaching water as well as on pH and the chemical balance at the solid-liquid interface. In particular, the majority of metals are released from the waste mass under acid conditions.

- pH: pH influences chemical processes which are the basis of mass transfer in the waste leachate system, such as precipitation, dissolution, redox and sorption reactions. It will also affect the speciation of most of the constituents in the system. Generally, acid conditions, which are characteristic of the initial phase of anaerobic degradation of waste, increase solubilization of chemical constituents (oxides, hydroxides and carbonated species), and decrease the sorptive capacity of waste.
- Redox potential: Reducing conditions, corresponding to the second and third phase of anaerobic degradation, will influence solubility of nutrients and metals in leachate.
- Landfill age. Landfill age obviously plays an important role in the determination of leachate characteristics governed by the type of waste stabilization processes.

# **Chapter 3 Materials and Methods**

# **3.1 INTRODUCTION**

There is already a lot of knowledge available in the literature on the biodegradation processes under landfill conditions as described in Chapter 2. However, due to complicate inter-reactions between physical, biological and chemical mechanisms, and the complexity of determination of biological parameters, the knowledge on the mechanisms of the biodegradation process under landfill conditions normally comes either from the empirical data from full-scale landfills or from laboratory-scale tests. Because of the uneasily predictable biodegradation process under landfill conditions, the experiments described in this chapter become necessary for both theory and practice. In addition, up to now there is no knowledge on the biodegradation of hospital waste pretreatment residues under landfill conditions, neither based on experiment nor from theory.

This paper emphasizes on the experimental data from laboratory tests of both municipal solid waste and hospital waste pretreatment residues, and later on looks into the mechanisms by modeling the biodegradation process based on the experimental data. Therefore, the description of experiments becomes a very important part of this thesis.

This chapter describes the materials and methods for the experiments, which is the basis for the discussion of the experimental data in the later chapters.

# **3.2 EXPERIMENTAL SETUP**

The experimental setup is presented in Fig. 3.1.

Three landfill reactors made of plastic columns were used for the first experiment for pure municipal solid waste (MSW), pure sterilized hospital waste (HSWs), and pure hospital waste incineration ash (HSWi).

The diameters and heights of these three column reactors are shown in Table 3.1.

	HSWs	MSW	HSWi
D(m)	0.283	0.210	0.285
H(m)	1	1	1

Table 3.1: Dimension of three Column Reactors

Three 120 I landfill reactors were constructed for the second experiment from plastic drums with approximately 0.40 m diameter by sealing the top, drilling outlets in the top for gas, temperature sensors and water distributors, and drilling outlets at the bottom for leachate. These three reactors are filled with municipal solid waste (MSW), mixture of sterilized hospital waste and municipal solid waste (MSW+HSWs), and mixture of hospital waste incineration ash and municipal solid waste (MSW+HSWi).

Leachate was collected in the bottom tank, and landfill gas was collected in aluminium gas bags at the top of each reactor. A peristaltic pump was used to deliver water from the container to the distributor at the top and to recycle the leachate from the bottom to the top.

All the reactors were placed in a constant temperature room (31-35°C). The temperature sensors are placed into the waste samples in order to check the temperature inside the landfilled waste.





G: gas bag T: temperature sensor P: pump W: bottom tank

## **3.3 WASTE SAMPLE PREPARATION**

3.3.1 Municipal Solid Waste Samples

Fresh municipal solid waste was collected and sorted. The waste composition was chosen according to the average values of typical municipal solid waste composition in the city of Duisburg in Germany.

The composition based on wet weight of the municipal solid waste for the first experiment is given in Table 3.2.

The composition based on wet weight of the municipal solid waste for the second experiment is given in Table 3.3.

Composition	MSW
Paper (%)	12.82
Glass (%)	4.78
Biodegradable material (%)	51.72
Package (%)	6.33
Others (%)	24.35
Total (%)	100

Table 3.2: Composition of Municipal Solid Waste for the First Experiment

Composition	MSW
Food (%)	25.7
Yard waste (%)	23.9
Paper (%)	19.3
Textile (%)	3.3
Plastic (%)	6.8
Glass (%)	12.2
Metal (%)	8.8
Total (%)	100

Table 3.3: Composition of Municipal Solid Waste for the Second Experiment

## 3.3.2 Sterilized Hospital Waste Samples

Sterilized hospital waste for the first experiment was taken from Universitaetsklinikum Duesseldorf, the biggest hospital in the German Federal State of Nordrhein-Westfalen. Sterilized hospital waste for the second experiment was taken from Universitaetsklinikum in the city of Muenster. The hospital waste used in the experiments is classified as C category – infectious hospital waste – according to German hospital waste management regulations. The sterilization process was carried out at 134°C and a steam pressure of 2 bar for 2 hours by autoclave.

The sterilized hospital waste was sorted and each waste fraction was measured by wet weight. The composition based on wet weight for the sterilized hospital waste is shown in Table 3.4.

Waste fraction	Composition
Paper (%)	14.3
Textile (%)	12.7
Plastic (%)	53.8
Glass (%)	19.2
Total (%)	100

Table 3.4: Composition of Sterilized Hospital Waste

#### 3.3.3 Hospital Waste Incineration Ash

The incineration of the hospital waste sample was carried out in a grate incinerator in "Abfallverwertung Augsburg" in the German Federal State of Bavaria. The incineration temperature was 850°C, and the total residence time of the batch process was 10 hours.

Fig. 3.2 shows the photo of the grate incinerator where the incineration of hospital waste was carried out.



Fig. 3.2: Photo of the Grate Incinerator for Hospital Waste

# 3.3.4 The Mixture of Sterilized Hospital Waste and Municipal Solid Waste

The sterilized hospital waste was mixed homogenous with municipal solid waste in the second experiment for the MSW+HSWs reactor, because in practice MSW and HSWs may be collected together.

# 3.3.5 The Mixture of Hospital Waste Incineration Ash and Municipal Solid Waste

The hospital waste incineration ash and municipal solid waste was put in the following way in the MSW+HSWi reactor: one layer of municipal solid waste after another layer of hospital waste incineration ash, because in practice there is a separated delivery of MSW and HSWi.

# **3.4 ANALYTICAL METHODS**

# 3.4.1 Weight of Waste

The weight of the wet waste and dry waste were measured by scale.

# 3.4.2 Water Content

A small portion of the wet waste fraction was measured by weight (M<sub>0</sub>) before it was put

into an oven at  $105^{\circ}$ C. Every 2 hours was taken out and the weight was measured until stable weight (M<sub>1</sub>) was reached. The water content can be calculated as:

Water content =  $(M_0 - M_1)/M_0$  (3.1)

# 3.4.3 Water Volume

Each bottom tank was calibrated by a measured water volume. The volume of leachate taken out and the new water added in was shown by the calibrated bottom tank.

# 3.4.4 Gas Volume

The gas was collected in aluminium gas bags allowing an over-pressure up to 0.3 bar. The gas volume was measured by displacement of an acid salt solution in a scaled cylinder.

The content of the acid salt solution is as following:

- -- 200 g NaCl per liter water
- -- 5 ml H2SO4
- -- 5 drop of methylorange (pH indicator)

The gas volume at STP can be calculated as following:

$$V(STP) = \frac{1.3 * V_m * 273}{(273 + T_m)}$$
(3.2)

where  $V_m$ ,  $T_m$  is measued gas volume and temperature.

The strong acid is added to avoid solution of CO<sub>2</sub> in water.

# 3.4.5 Gas Compostion

The gas composition was analyzed with a *Unicam* 610 series gas chromatograph using a "Porapack Q" column by *J&W Scientific*.

One example of the analytical graphs from the gas chromatograph is shown in Fig. 3.3.

The first peak is  $N_2+O_2$ , the second peak is  $CH_4$ , and the third peak is  $CO_2$ . The composition of each gas component can be calculated as following:

$$Composition = \frac{Area_i}{\sum Area_i}$$
(3.3)



Fig. 3.3 Analytical Graph for Gas Composition from Gas Chromatograph

# 3.4.6 Fatty Acid Concentration

Fatty acids need 4 hours extraction by diethyl ether in a water bath heating system. The sketch of the extraction device is shown in Fig. 3.4.



Fig. 3.4: Sketch for Fatty Acids Extraction

The procedure of extraction is as following:

- Wash the water cooling system with diethyl ether.
- -- Wash the big flask with distillated water and alcohol, then dry it and put three or four pieces of boiling stones into the small flask. Then weigh it with the electronic scale (M1).
- -- Take about 100 ml leachate sample into the big flask, then weigh the big flask with the sample (M2).
- Put about 10 drops phosphoric acid into the big flask.
- -- Wash the small flask with distillated water and alcohol, then dry it and weigh it with electronic scale (M3).
- Connect the water cooling system, small flask and big flask. Small flask is put into the water keeping a temperature of about 50°C.
- Open the valve for cooling water
- -- Add 40 ml diethyl ether into the big flask and form a recycle system.
- -- 4 or 5 hours later, there are some extractions in the small flask and weigh it (M4).

- Take some sample from extractions (M5), and add some standard butanol (C= 4.374 g/l) into it(M6).

-- Add a little bit of Na<sub>2</sub>SO<sub>4</sub> into the sample for absorbing the water.

The extracted organic fatty acids in the leachate were determined with the same *Unicam* 610 series gas chromatograph using a "FFAP" column by *J&W Scientific*.

One of the analytical graphs for fatty acids concentration is shown in Fig. 3.5.

The calculation of the fatty acids concentration is shown in equation 3.4.

$$C_{i,ether} = 4.374 * \frac{Area_i}{Area_{bu \tan ol}} * \frac{M6}{M5}$$

$$C_{i,water} = C_{etheri} * \frac{(M4 - M3)}{(M2 - M1)} * \frac{\rho_{water}}{\rho_{ether}}$$
(3.4)

where  $\rho_{water}$ ,  $\rho_{ether}$  is the density of water and ether, respectively,  $C_{i,ether}$  and  $C_{i,water}$  is the fatty acids concentration of i component respecting to ether and water, respectively.


Fig. 3.5: Analytical Graph for Fatty Acids Concentration from Gas Chromatograph

# 3.4.7 pH

The pH value of the leachate was measured with a CG840 pH meter.

The principle of electrometric pH measurement is the determination of the activity of hydrogen ions by potentiometric measurement. The measured electrode potential changes linearly with pH.

In common case, buffer solutions are needed for calibration. There are typically two kinds of buffer solutions depending on the expected pH: We used a solution of pH 6.88 (di-sodium hydrogen phosphate) and a solution of pH 4.01 (potassium hydrogen phosphate).

Since pH value is temperature dependent, a temperature compensating device is needed.

A complete pH meter should be consisting of potentiometer, a glass electrode, a reference electrode, and a temperature compensating device.

### 3.4.8 Chemical Oxygen Demand

COD was analyzed using oxidation by Cr(VI) and a photometric method (photometer

SQ118 by *Merck*). The extent of sample oxidation may be affected by digestion time and sample COD concentration. In the experiment, the samples were oxidized with a solution of potassium dichromate, with silver sulfate (AgSO<sub>4</sub>) as a catalyst especially for organic compounds.

COD is a defined test. The method is analogous to EPA 410.4, US Standard Methods 5220 D, and ISO 15705.

# 3.4.9 Ammonium Nitrogen

Ammonium-nitrogen was detected by a *Merck* Spectroquant test using the SQ118 photometer.

The principle of this method is a colour reaction. Following adjustment to pH 13, ammonia reacts with hypochlorite to monochloramine, which in turn forms a blue indophenol dye in a catalysed 2-stage reaction with thymol. Spectrophotometers show linear absorbance in accordance with Lambert-Beer's Law to  $NH_4^+$ .

# 3.4.10 Anion Concentration

The anion concentration such as sulphate and chloride was simply measured by test papers.

# 3.4.11 Conductivity

The conductivity of the leachate was measured by a WTW LF92 conductivity meter.

Conductivity is a measure of water's ability to conduct electric current. The more total dissolved solids are in water, the greater is electric conductivity. Temperature will affect conductivity and must be compensated by the conductivity meter. Conductivity is measured in µS/cm or mS/cm.

# 3.4.12 ICP Test of the Leachate

Inductive Coupled Plasma (ICP) is a standard method for elementary analysis.

This ICP test was carried out in Analytisches Labor Gesenkirchen. The standard is DIN38406E22.

# Chapter 4 Biodegradation of Sterilized Hospital Waste in comparison with Municipal Solid Waste

### **4.1 INTRODUCTION**

Sterilization is a cheap way to treat hospital waste. This technique can provide the same level of pathogen destruction without the problem of dioxin emission and flue gas cleaning connected with incineration. However, public concerns about this technique must include the fate of residues after sterilization. Landfilling of the residues is the most common way of final disposal of hospital waste after sterilization. The knowledge of biodegradation of hospital waste naturally becomes important for landfill operators. No research work was ever done on this field. This chapter starts the research on biodegradability of sterilized hospital waste residues in comparison with municipal solid waste. With this knowledge, landfill operators may decide the suitable deposit cell for hospital waste or whether it is necessary to dump hospital waste into a separate cell.

# 4.2 WASTE CHARACTERISTICS OF STERILIZED HOSPITAL WASTE IN COMPARISON WITH MUNICIPAL SOLID WASTE

# 4.2.1 Comparison between Composition of Sterilized Hospital Waste and Municipal Solid Waste

Sterilized hospital waste was sorted. Each fraction of waste components was measured by wet weight. Municipal solid waste was composed according to the statistic household waste composition of Duisburg city.

Table 4.1 shows the waste composition.

composition	HSWs	MSW
paper(%)	14.30	12.82
glass(%)	19.20	4.78
food and yard waste(%)	0	51.72
plastic(%)	53.80	6.33
textile(%)	12.70	0
others	0	24.35
total(%)	100	100

Table 4.1: Composition of Sterilized Hospital Waste and Municipal Solid Waste

The wet weight of sterilized hospital waste and municipal solid waste was 9.827 kg and 8.745 kg respectively. The dry weight of sterilized hospital waste and municipal solid waste was 9.43 kg and 5.86 kg respectively.

### 4.2.2 Hydraulics of Landfill Reactors

For the simulation, a precipitation of 750 mm/a is chosen according to the average precipitation of west Germany. On the actual landfill site, when the rain passes a unit of following properties: 1 m<sup>2</sup> area, 20m height, 1 Mg/m<sup>3</sup> dry density, the leachate is 40% of the precipitation <sup>[16]</sup>. Then the actual rain/dry waste ratio can be calculated in the following:

$$Q = \frac{40\% * 750l/a}{1*20*1000kg} = 0.015l/(kg*a)$$
(4.1)

The acceleration factor in simulation is chosen as 240. Then in the simulation the rain/dry waste ratio is 3.6 l/(kg\*a) for the landfill reactors.

In the sterilized hospital waste simulation landfill reactor, this leads to the volume of exchange water to be 34 l/a. Every 10 days 900 ml leachate is taken for sampling, and the same amount of new water is added.

In the municipal solid waste simulation landfill reactor, the volume of exchange water should be 21 l/a. Every 10 days 500 ml leachate is taken for sampling, and the same amount of water is added.

The water content of the waste was initially adjusted to 65%.

From 130 days on, 2-4 I leachate was recycled everyday.

# 4.2.3 Comparison between Biodegradable Organic Carbon Content of Hospital Waste and Municipal Solid Waste

The water content, carbon content and biodegradability factors of each waste fraction was chosen from empirical data <sup>[17]</sup>, and is shown in Table 4.2.

	kg H <sub>2</sub> O/kg wet	kg C/kg dry		kg Biodg.C/kg
waste component	component	component		С
food waste	0.6		0.48	0.8
yard waste	0.5		0.48	0.7
paper and				
cardboard	0.08		0.44	0.5

plastics and rubber	0.02	0.7	0
textiles	0.1	0.55	0.2
wood	0.2	0.5	0.5
glass	0.03	0	0
metals	0.03	0	0

Table 4.2: Empirical Waste Parameters

The evaluation of the biodegradable organic carbon was carried out according to:

$$(OC_b)_i = (OC)_i * (f_b)_i * (1 - u_i) * p_i$$
 (4.2)

where:

 $(OC_b)_i$ , the biodegradable organic carbon in the *i*th component of waste, kg biodegradable carbon

(OC)<sub>i</sub>, the organic carbon content in the dry *i*th component of waste, kg C/kg dry *i* component

 $(f_b)_i$ , biodegradable fraction of OC<sub>i</sub>, kg biodegradable carbon/kg carbon

ui, the moisture content of the *i*th component of waste, kg water/kg wet *i* component

pi, the wet weight of the *i*th component of waste, kg wet *i* component

The sterilized hospital waste: 0.042kg biodegradable carbon per kilo dry waste.

The municipal solid waste: 0.157kg biodegradable carbon per kilo dry waste.

Table 4.3 summarizes the calculation results.

Biodegradable carbon content of MSW	Biodegradable carbon content of HSWs
0.157 kg Biod.C/kg dry waste	0.042 kg Biod.C/kg dry waste

Table 4.3: Biodegradable Carbon Content of Municipal Solid Waste and Sterilized Hospital Waste

# 4.2.4 Maximum Gas Prediction

A reaction representing the overall methane fermentation process for organics in solid waste can be represented by the following equation <sup>[17]</sup>:

 $C_aH_bO_cN_d + nH_2O \rightarrow xCH_4 + yCO_2 + wNH_3 + zC_5H_7O_2N + energy$  (4.3) Where  $C_aH_bO_cN_d$  is the empirical chemical formulation for biodegradable organics in solid waste, and  $C_5H_7O_2N$  is the chemical formulation of bacterial cells.

The biodegradable organic carbon found in MSW is transformed during anaerobic degradation into methane and carbon dioxide. The energy content of the organic matter is split into the free energy content of methane,  $CO_2$  and  $NH_3$ , the energy for bacterial metabolism, and enthalpy of the reaction.

The fraction of the organic matter that is converted to biomass, considering an infinite reaction time in the system, is about 4%. Therefore, for the practical evaluation of the maximum theoretical landfill gas yield, cell conversion of organic matter can be neglected, and equation (4.3) becomes:

$$C_{a}H_{b}O_{c}N_{d} + \frac{4a-b-2c+3d}{4} \cdot H_{2}O \rightarrow \frac{4a+b-2c-3d}{8} \cdot CH_{4} + \frac{4a-b+2c+3d}{8} \cdot CO_{2} + dNH_{3}$$

$$(4.4)$$

Once the elementary composition of the waste is known, this equation permits evaluation of both the quantity and quality of the gas  $(CH_4+CO_2)$  generation.

Table 4.4 summarizes some typical data on the elementary composition of the waste fraction of MSW <sup>[18]</sup>.

Component		Ρ	ercent l	by weig	ht	
	С	Н	0	Ν	S	Ash
Organic						
Food	48.0	6.4	37.6	2.6	0.4	5.0
Paper	43.5	6.0	44.0	0.3	0.2	6.0
Cardboard	44.0	5.9	44.6	0.3	0.2	5.0
Plastics	60.0	7.2	22.8			10.0
Textiles	55.0	6.6	31.2	4.6	0.15	2.5
Rubber	78.0	10.0		2.0		10.0
Leather	60.0	8.0	11.6	10.0	0.4	10.0
Yard waste	47.8	6.0	38.0	3.4	0.3	4.5
Wood	49.5	6.0	42.7	0.2	0.1	1.5
Inorganic						
Glass	0.5	0.1	0.4	<0.1		98.9
Metals	4.5	0.6	4.3	<0.1		90.5
Dirt,ash,etc.	26.3	3.0	2.0	0.5	0.2	68.0

Table 4.4: Elementary Composition of MSW

The theoretical gas amount can be calculated in following steps:

• Step 1:

The dry weight of biodegradable organics can be calculated by the following equation

biodegradable dry weight= dry weight  $\cdot$  biodegradability factor (4.5) The biodegradable organics of the MSW is 1.963kg.

The biodegradable organics of the sterilized hospital waste is 0.871 kg.

• Step 2:

Combining the result of step 1 and table 4.4, the percentage distribution of the elements can be achieved.

Percentage distribution of the major elements composing the MSW and HSWs is shown in Table 4.5:

Component	C (kg)	H (kg)	O (kg)	N (kg)
HSWs	0.405	0.054	0.355	0.122
MSW	0.919	0.124	0.771	0.039

Table 4.5: Percentage Distribution of Biodegradable Organics of MSW and HSWs

• Step 3:

Determine an approximate chemical formula by relating to N:

The chemical formula for MSW is: C27.4H44.2O17.2N

The chemical formula for HSWs is: C<sub>32.98</sub>H<sub>4.37</sub>O<sub>28.89</sub>N

• Step 4:

Suppose the chemical reaction equation as:

$$C_a H_b O_c N_d + x H_2 O \rightarrow y C H_4 + z C O_2 + n N H_3$$
(4.6)

Then:

$$x = (4a-b-2c+3d)/4 = 8.5$$
  
y = (4a+b-2c-3d)/8 = 14.5  
z = (4a-b+2c+3d)/8 = 12.8  
n = d = 1

The volume of methane and carbon dioxide produced:

$$V_i = \frac{Bio.Organics}{Mole.weight} \bullet n_i RT / P$$
(4.7)

Where R=8.34

T=273.15K

P=101300pa

Bio.Organics is the result from step 1

Mole.weight is the molecular weight of the formula from step 3

 $n_i$  is the value of y, z for CH<sub>4</sub> and CO<sub>2</sub>, respectively

Total theoretical amount of gas generated per unit dry weight of MSW:

V=0.312m<sup>3</sup>/kg dry waste

Total theoretical amount of gas generated per unit dry weight of sterilized hospital waste:

V=0.078m<sup>3</sup>/kg dry waste

Table 4.6 summarizes the result for theoretical maximum gas amount for MSW and HSWs.

Maximum gas production for MSW	Maximum gas production for HSWs
0.312 m <sup>3</sup> /kg dry waste	0.078 m <sup>3</sup> /kg dry waste

Table 4.6: Theoretical maximum gas production for MSW and HSWs

# 4.3 BIODEGRADATION PROCESS OF STERILIZED HOSPITAL WASTE IN COMPARISON WITH MUNICIPAL SOLID WASTE

# 4.3.1 Gas Production of Sterilized Hospital Waste in Laboratory Test





Fig. 4.1: Gas Production of HSWs in Comparison with MSW

The accumulative gas amount of sterilized hospital waste is only 1.27 l/kg dry waste, and 29.41 l/kg Biod.C. The accumulative gas amount of municipal solid waste is 11.69 l/kg dry waste, and 74.30 l/kg Biod.C.

The municipal solid waste produces approximately 9 times gas compared to sterilized hospital waste.

Compared with the theoretical gas amount, only 1.63% biodegradable organics is biodegraded in the sterilized hospital waste landfill reactor after 160 days of simulation time.

Compared with the theoretical gas amount, 3.75% biodegradable organics is biodegraded in the municipal solid waste landfill reactor after 160 days of simulation time.

In summary, the municipal solid waste produces much more gas than sterilized hospital waste. On the one hand this is due to the higher amount of biodegradable organics content, on the other hand it is due to better bacteria biological reactivity in the municipal solid waste than in the sterilized hospital waste. The hospital waste after sterilization is not easy for inoculation of bacteria because of high content of plastics and glass and low content of biodegradable organic material.

From 130 days on, leachate was recycled in both reactors. It is observed that the gas amount increases four times in the MSW reactor, while no more gas was generated in the sterilized hospital waste due to no active bacteria. It indicates that single pass of water in waste is not sufficient for organics decomposition. There is still a large amount of biodegradable material undegraded both in MSW and HSWs reactors. Leachate recycling will enhance the stabilization in a moderate climate like in west Germany.

#### 4.3.2 Gas Composition

Fig. 4.2 illustrates the gas development in the HSWs and MSW reactors.

Methane development in both reactors is quite similar. Methane starts to generate on 30th day in both reactors and both need 140 days to reach 50% of methane. That means the lag time for the methane generation is 30 days.

The CO<sub>2</sub> reaches a higher concentration in the MSW reactor, which may due to the higher content of organic materials for aerobic decomposition than in the HSWs reactor.

From the gas compositions of HSWs and MSW reactors, the different biodegradation phases can be clearly identified:

-From 0 to 10 days, it is an aerobic phase for both reactors.  $CO_2$  starts generation and  $O_2$  starts to decrease.

-From 10 to 30 days, it is a first intermedial anaerobic phase in both reactors. It is characterized by rapid generation of  $CO_2$  and decrease of  $O_2$ .

-From 30 to 140 days, it is a second intermedial anaerobic phase in both reactors with growth of methanogenic bacteria. The methane concentration gradually increases to 50% while  $CO_2$  concentration gradually decreases to 50%.

-From 140 days on, it is methane phase in both reactors. A stable methane concentration of 55% maintains.

From the results, it can be concluded that landfill gas composition development of sterilized hospital waste is similar as of the municipal solid waste. The sterilized hospital waste generates a smaller amount of landfill gas than the municipal solid waste, but the quality of the landfill gas is the same as that of municipal solid waste.

This result may indicate that sterilized hospital waste has the same biodegradation processes as municipal solid waste, but the gas production amount and rate is lower than municipal solid waste due to smaller amount of biodegradable material and worse conditions for bacteria inoculation.

40







41



Fig. 4.2: Gas Composition of HSWs and MSW

### 4.3.3 PH-value of Leachate

Fig. 4.3 illustrates the pH value of the leachates from the HSWs and MSW reactors.

pH decreases to 5 in both reactors within 20 days. The hydrolysis of organics into fatty acids results in a low pH value. Under these conditions, methanogenic bacteria are inhibited. Later, with the growth of methanogenic bacteria and the conversion of fatty acids into methane, pH gradually increases to around 7 in the HSWs reactor and 6 in the MSW reactor.

The pH value is a little higher in the HSWs reactor than in the MSW reactor. The reason is that there is lower fatty acids concentration in the HSWs reactor due to lower content of organics inside the waste materials than in the MSW reactor.



Fig. 4.3 PH value of the leachate

### 4.3.4 COD of the Leachate

Fig. 4.4 shows the COD concentration of the leachate from the HSWs reactor and MSW reactor.



Fig4.4 COD of the Leachate

Comparing the COD loads, clearly much higher COD is observed for the municipal solid waste landfill reactor than in the sterilized hospital waste landfill reactor. From this point, sterilized hospital waste has lower organic load on leachate treatment.

Both reactors show a decreasing concentration of COD with time. This effect may result from an overlapping of two effects. On the one hand there is biodegradation. On the other hand physical-chemical solution of water-soluble compounds takes place. According to experience, the solution effect decreases rapidly with time, while biodegradation may continue for a longer time period.

# 4.3.5 Ammonium Concentration of the Leachate

Fig. 4.5 illustrates the ammonium concentration of the leachate.



Fig. 4.5: Ammonium Concentration of the Leachate

As a result of decomposition of organic matter containing nitrogen, initial concentrations increased both in the municipal solid waste landfill reactor and in the sterilized hospital waste landfill reactor.

Ammonium concentration appears to a peak on 80th day in both reactors, which might be the high rate time for decomposition of proteins. After this peak time, ammonium gradually decreases with time.

The ammonium concentration is higher in the municipal solid waste, which may result from the higher amount of proteins in the municipal solid waste compared to the sterilized waste.

# 4.3.6 Fatty Acids Concentration of the Leachate

# • Sum of Fatty Acids

The sum of fatty acids concentration of the leachates from HSWs and MSW reactors is shown in Fig. 4.6.



Fig. 4.6: Sum of Fatty Acids Concentration

Fatty acids concentration reaches a highest value around 30 to 50 days and results lowest pH value in both reactors. At this time, little methane is generated. After 50 days, accompanying with quick growth of methanogenic bacteria and their conversion of the fatty acids to methane, methane production increases, pH value starts to increase, fatty acids concentration decreases dramatically. Later, following with decomposition of organics, fatty acids concentration gradually decreases with time.

After starting leachate recycling, fatty acids concentration rises again in the MSW reactor due to increasing hydrolysis rate with higher moisture content.

# • Acetic Acid Concentration of the Leachate

Fig. 4.7 shows acetic acid concentration of the leachate from HSWs and MSW reactor.



Fig. 4.7: Acetic Acid Concentration of the Leachate

Acetic acid concentration reaches highest concentration on 30 to 50 days in both reactors. After 50 days, following with the growth of methanogenisis bacteria, acetic acid concentration decreases to a very low value, which may mean the methanogenesis process might not be the limiting step of the whole biodegradation process. Hydrolysis or acetogenesis may become the limiting step of the biological reaction.



### Butyric Acid Concentration

Fig. 4.8: Butyric Acid Concentration of the Leachate

Fig. 4.8 illustrates the butyric acid concentration in both reactors.

Butyric acid concentration reaches highest value also on 30 to 50 days in both reactors

and decreases after 50 days when methane production increases.

Here it must be pointed out that the butyric acid concentration in the same period of time is much higher than acetic acid concentration or any other type of fatty acids in both reactors. This may indicate that the conversion from butyric acid to acetic acid might become the rate controlling step of biodegradation process.

After leachate recycling, the butyric acid concentration in the MSW reactor rises because of the higher hydrolysis rate resulting from increasing moisture content.

# Chapter 5 Co-disposal of Sterilized Hospital Waste with Municipal Solid Waste

### **5.1 INTRODUCTION**

Chapter 4 described the biodegradability of sterilized hospital waste in comparison with municipal solid waste. Separated disposal of sterilized hospital waste by landfilling was simulated. The results indicate the bad conditions of sterilized hospital waste for bacteria inoculation causes poor degradation of organics in the landfill reactor. Therefore, this chapter goes further to the investigation of co-disposal of sterilized hospital waste with municipal solid waste. With this knowledge, landfill operators may realize whether it is advantageous to mix sterilized hospital waste affects the gas emission and leachate quality of a household waste landfill site.

# 5.2 WASTE CHARACTERISTICS OF THE MIXTURE OF STERILIZED HOSPITAL WASTE AND MUNICIPAL SOLID WASTE

# 5.2.1 Composition of Sterilized Hospital Waste and Municipal Solid Waste

Table 5.1 shows the waste compositions of sterilized hospital waste and municipal solid waste in this experiment.

Composition	HSWs	MSW
Food (%)	0	25.7
Yard waste (%)	0	23.9
Paper (%)	14.3	19.3
Textile (%)	12.7	3.3
Plastic (%)	53.8	6.8
Glass (%)	19.2	12.2
Metal (%)	0	8.8
Total (%)	100	100

Table 5.1: Composition of Sterilized Hospital Waste and Municipal Solid Waste

Sterilized hospital waste and municipal solid waste are separately composed by wet weight at first. Then 5.174 kg of wet sterilized hospital waste is taken and homogenously mixed with 8.22 kg of wet municipal solid waste in one reactor. In parallel, 17.37 kg pure municipal solid waste is filled in another reactor.

# 5.2.2 Hydraulics of Landfill Reactors

The rain ratio is kept the same as 3.6 l/(kg\*a). 1 I leachate was taken out for sampling and the same amount of new water was added in every 10 days in the mixture of sterilized hospital waste and municipal solid waste landfill reactor (HSWs+MSW). 1.2 I leachate was taken out for sampling and the same amount of new water was added in every 10 days in the pure municipal solid waste (MSW) reactor.

8-10 I leachate was recycled every day in both reactors.

# 5.2.3 Biodegradable Carbon Content

Equation 4.2 was used for the mixture of sterilized hospital waste and municipal solid waste, and for pure municipal solid waste.

The biodegradable carbon content of the mixture of sterilized hospital waste and municipal solid waste is 0.114 kg Biod.C/kg dry waste.

The biodegradable carbon content of the pure municipal solid waste is 0.174 kg Biod.C/kg dry waste.

# 5.2.4 Maximum Gas Amount Prediction

The same procedures of calculation as in chapter 4.2.4 are carried out for the HSWs+MSW reactor and the MSW reactor.

The biodegradable dry weight of organics in the MSW reactor is 4.527kg.

The percentage distribution of the major elements composing the MSW is shown in Table 5.2:

Component	C (kg)	H (kg)	O (kg)	N (kg)
MSW	2.108	0.278	1.800	0.096

Table 5.2: Percentage Distribution of Biodegradable Organics of MSW

The chemical formula for MSW is:  $C_{25.6}H_{40.6}O_{16.4}N$ Suppose the chemical reaction equation 4.6 Then: x = (4a-b-2c+3d)/4=8.0y = (4a+b-2c-3d)/8=13.4 z = (4a-b+2c+3d)/8=12.23 n = d = 1

The volume of methane and carbon dioxide produced can be calculated with equation 4.7: Total theoretical amount of gas generated per unit of dry weight of MSW:

V=0.356m<sup>3</sup>/kg dry waste

Total theoretical amount of gas generated per unit of dry weight of sterilized hospital waste is the same as in chapter 4:

V=0.078m<sup>3</sup>/kg dry waste

For the mixture of sterilized hospital waste and municipal solid waste:

$$V = \frac{0.356 * 5.754 + 4.967 * 0.078}{5.754 + 4.967} = 0.227m^3 / kg \ dry \ waste$$

# 5.3 CO-DISPOSAL OF STERILIZED HOSPITAL WASTE WITH MUNICIPAL SOLID WASTE IN LABORATORY TEST

# 5.3.1 Gas Production

Fig. 5.1 shows the gas production in HSWs+MSW and MSW landfill reactors. The accumulative gas production on 160 days simulation for HSWs+MSW and MSW is 113 l/kg dry waste and 120 l/kg dry waste, respectively. The accumulative gas amount dependent on biodegradable carbon is 1002 l/kg Biod.C and 689 l/kg Biod.C respectively in HSWs+MSW reactor and MSW reactor. Compared with theoretical gas amount, 50% biodegradable material was degraded in the HSWs+MSW reactor, and 34% biodegradable material was degraded in the MSW reactor.







This means, although the accumulative gas production is less in the HSWs+MSW reactor due to less biodegradable material than that of the MSW reactor, a higher percentage of biodegradable material was degraded in the HSWs+MSW reactor than in the MSW reactor. This may indicate an enhancement of biodegradation.

The mechanism may be explained by "dilution effect". The acidogenisis of organics results in a low pH value and in a "conservation process". Under these conditions the fermentating hydrolysis bacteria and methane producing bacteria are not able to develop. In the mixture of sterilized hospital waste and municipal solid waste, the lower organic content in hospital waste may dilute the higher organic content in municipal solid waste, which might be advantageous to decrease the organic acids concentration and thus enhance the biodegradation process.

The dilution of organics by sterilized hospital waste may also provide a wider surface area for mass transport, which might also result in the enhancement of sterilized hospital waste degradation.

Compared with the biodegradation of pure sterilized hospital waste described in chapter 4, the biodegradation of the mixture of sterilized hospital waste and municipal solid waste is not only better than pure municipal solid waste, but also better than pure sterilized hospital waste. This can be explained by the better conditions for bacteria inoculation for sterilized hospital waste when it is mixed with municipal solid waste.

From this point, it can be concluded that co-disposal of sterilized hospital waste with municipal solid waste is advantageous for the stabilization of a household waste landfill site.

#### 5.3.2 Gas Composition





Fig. 5.2: Gas Composition of HSWs+MSW and MSW Reactor

Fig. 5.2 illustrates the gas composition development of HSWs+MSW and MSW reactors. The lag time for methane procuction for both reactors is 30 days, the same as for the pure sterilized hospital waste landfill reactor and for the municipal solid waste landfill reactor in chapter 4. It needs 95 days to reach 50% methane in the municipal solid waste reactor and it needs 120 days to reach 50% methane in HSWs+MSW reactor. This proves the pure sterilized hospital waste, the pure municipal solid waste both in chapter 4 and in this experiment, as well as the mixture of sterilized hospital waste and municipal solid waste has the same lag time and a similar methane developing process. This may indicate that lag time and the methane developing rate do not depend on the waste composition within a certain range. To a great extent they may depend on the external environmental conditions such as oxygen, pH and alkalinity, temperature, moisture. When these conditions keep the same, the biochemical reaction rate keeps the same.

Sterilized hospital waste does not affect the lag time and methane developing rate, but it promotes the gas amount by dilution of organics and providing a wide surface area for organic mass transport. From this point of view, sterilized hospital waste is advantageous for household landfill site stabilization. Therefore, it is recommended to co-dispose sterilized hospital waste with municipal solid waste.

The CO<sub>2</sub> concentration of the MSW reactor is a little higher than that of HSWs+MSW reactor. This may be due to a higher content of organics for aerobic decomposition of municipal solid waste compared to the mixture of sterilized hospital waste and municipal solid waste.

From the gas compositions of HSWs+MSW and MSW reactors, the following phases can be identified:

From 0 to 10 days, there is an aerobic phase for both reactors. It is characterized by  $CO_2$  generation and  $O_2$  decrease.

From 10 to 30 days, there is a first intermedial anaerobic phase in both reactors. It is characterized by rapid generation of  $CO_2$  and decrease of  $O_2$ .

From 30 to 95 days, it is a second intermedial anaerobic phase in MSW reactor. From 30 to 120 days it is a second intermedial anaerobic phase in MSW+HSWs reactor. With growth of methanogenic bacteria, the methane concentration gradually increases to 50%.

From 95 days on in MSW reactor and from 120 days on in MSW+HSWs reactor, it is methane phase in both reactors. A stable methane concentration of 55% is maintained.

From the results, it can be concluded that landfill gas composition development of the mixture of sterilized hospital waste and municipal solid waste is similar as of the pure municipal solid waste. The quality of the landfill gas of mixture of sterilized hospital waste is the same as that of pure municipal solid waste.

#### 5.3.3 PH-value of Leachate



Fig. 5.3: PH-value of the Leachate from HSWs+MSW and MSW Reactors

Fig. 5.3 illustrates the pH values of the leachate from HSWs+MSW and MSW reactors. It is shown that the pH is nearly the same in both reactors. This indicates that sterilized hospital waste does not affect the pH value of the leachate of household landfill site.

This gives a hint that the enhancement of gas production does not result from the dilution effects of lower organic acids content sterilized hospital waste on municipal solid waste, but probably results from the wider surface area for organic mass transport

### 5.3.4 COD of Leachate



Fig. 5.4: COD concentration of HSWs+MSW and MSW Reactors

Based on the experimental results in chapter 4, a continuous decrease of COD concentration is expected in each reactor with simulation time. Therefore, in the second experiment in this chapter, COD concentration is only detected from 0 to 43 days. Fig. 5.4 illustrates the COD concentration in the HSWs+MSW reactor and MSW reactor.

It is shown that the COD concentration in both reactors is nearly the same, which once more proves that sterilized hospital waste does not affect the leachate quality of household waste landfill site, neither with respect to pH value nor to COD concentration. Combined with the results in Chapter 4, this may be a hint on that no matter disposal of sterilized hospital waste separately or co-disposal with municipal solid waste, the mechanism of biodegradation process and the rate of biodegradation might be similar. Sterilized hospital waste does not affect the quality of leachate and landfill gas, but it may affect the total gas amount of the municipal solid waste due to dilution of the organic material and thus result in a wider surface area for mass transport.

### 5.3.5 Ammonium Concentration of the Leachate

Fig. 5.5 illustrates the ammonium concentration of the leachates from HSWs+MSW and MSW reactors.

It can be seen that the ammonium concentration is higher in the MSW reactor than in the HSWs+MSW reactor. This is due to the higher content of organics containing nitrogen such as proteins inside the municipal solid waste than that in the mixture of sterilized hospital waste and municipal solid waste.



Fig. 5.5: Ammonium Concentration of the Leachate

# 5.3.6 Fatty Acids Concentration of the Leachate

Table 5.3 shows the fatty acid concentrations on 10th day of HSWs+MSW and MSW reactors.

The fatty acids concentration is similar in both reactors. This is correspondent to the similar pH value of the leachate in both reactors. This is another proof that the dilution of fatty acids is excluded in the case of sterilized hospital waste. The gas enhancement of the mixture of

	MSW(mg/l)	MSW+HSWs(mg/l)
Acetic acid	107	80
Propionic acid	60	251
Butyric acid	336	243
Isovaleric acid	26	14
n-valeric acid	9	7
Caproic acid	4	26
Hexanoic acid	39	26
Nanoic acid	19	28
Total	720	847

Table 5.3: Fatty Acids Concentration in MSW and MSW+HSWs Reactors

sterilized hospital waste and municipal solid waste might result from the wider surface area for organic mass transport.

In the MSW and MSW+HSWs reactors, butyric acid is the main kind of fatty acids. It indicates the conversion from butyric acid to propionic acid or acetic acid may be the limiting step of biodegradation in these two reactors.

# Chapter 6 Leaching Behavior of Hospital Waste Incineration Ash and Co-disposal with Municipal Solid Waste

### **6.1 INTRODUCTION**

Incineration ash was thought to be hazardous waste and needs special care for final disposal because of the problems of dioxins and heavy metal. Some research was done already on the leaching behavior of pure incineration ash, but no investigation was ever done on the effects of incineration ash on municipal solid waste biodegradation process when it is mixed with municipal solid waste. No data is available to show whether incineration ash is advantageous or dangerous for biochemical reactions under landfill conditions. This chapter deals with not only the leaching behavior of hospital waste incineration ash, but also the effects of incineration ash on a household waste landfill site. With the results, a novel approach to treat incineration ash will be concluded.

### 6.2 THE LEACHING BEHAVIOR OF HOSPITAL WASTE INCINERATION ASH

# 6.2.1 Waste Characteristics and Hydraulics of Hospital Waste Incineration Ash Landfill Reactor

26.182 kg of dry hospital waste incineration ash was filled in one landfill simulation reactor. The same hydraulics described in Chapter 4 was chosen for the incineration ash landfill reactor. Every 10 days 2.5 I leachate was taken out for sampling, and the same amount of new water was added.

### 6.2.2 Results and Discussions

# Inductive Coupled Plasma (ICP) Detection of the Leachate from Hospital Waste Incineration Ash

Table 6.1 shows the ICP detection results of the leachate from the hospital waste incineration ash (HSWi) reactor in comparison with the leachate from the sterilized hospital waste (HSWs) and municipal solid waste (MSW).

It can be seen that the calcium, magnesium and manganese concentration is much higher in the hospital waste incineration ash reactor than in the other two. The sodium and potassium concentration of the leachate from the sterilized hospital waste landfill reactor is much lower than that from the municipal solid waste landfill reactor which contains food waste. The food waste might be the source of the high concentration of sodium and potassium.

	HSWs(mg/l)	HSWi(mg/l)	MSW(mg/l)
Na	220	2000	20000
К	180	1400	3200
Mg	77	280	0.21
Са	620	4500	2.8
AI	3.3	0.93	70
Sn	<0.005	0.045	<0.005
Pb	0.004	0.008	<0.002
As	0.019	0.034	0.071
Hg	<0.002	<0.002	<0.002
Sb	0.035	0.012	0.17
V	0.029	0.017	0.26
Cr	0.020	0.036	0.38
Mn	6.1	17	<0.005
Fe	74	10	0.11
Со	0.13	0.15	0.10
Ni	0.15	0.28	0.17
Cu	0.25	0.038	7.2
Zn	11	1.9	0.034
Cd	0.0023	0.0024	0.0005
Р	63	84	18

The heavy metal concentrations in the leachates from all the three reactors are rather low. This is a hint that incineration ash has not a serious heavy metal leaching problem.

Table 6.1: ICP Test of Leachate from HSWi, HSWs and MSW Landfill Reactors

# • Landfill Gas Production

Only a negligible amount of gas generated at the very beginning, and there was no gas generation later on from the hospital waste incineration ash reactor because there is no biodegradable organics available. In case the organics in the waste were not completely incinerated, there might be a very small amount of landfill gas generation.

 PH Value of the Leachate from Hospital Waste Incineration Ash in Comparison with Municipal Solid Waste

Fig. 6.1 illustrates the pH value of the leachate of the hospital waste incineration ash landfill

reactor in comparison with the municipal solid waste (MSW) landfill reactor described in Chapter 4.

The pH value of the incineration ash reactor increase to 13.2 from beginning on, and keep at 12-13 during all the time. In contrast, the pH of the leachate from the municipal solid waste decreases to 5.16 and keeps acid all the time.

The incineration ash under landfill conditions shows a completely different leaching behavior compared to municipal solid waste. The pH-value of the leachate of the ash landfill reactor is alkaline. This is due to dissolution of alkaline reacting compounds, as for example metal oxides and their salts, hydroxides and carbonates content inside the incineration ash, such as Na<sub>2</sub>O, K<sub>2</sub>O, CaO or CaCO<sub>3</sub> etc.



Fig. 6.1 PH Value of the Leachate of HSWi Reactor in Comparison with MSW Reactor

• COD Concentration of the Leachate from the Hospital Waste Incineration Ash in Comparison with Municipal Solid Waste

Fig. 6.2 illustrates the COD concentration of the leachate from HSWi reactor in comparison with MSW reactor. The COD concentration of HSWi reactor is much lower than that of MSW reactor. This indicates that incineration ash has much lower organics load on the leachate treatment than municipal solid waste.



Fig. 6.2: COD of the Leachate from HSWi and MSW Reactors

# • Ammonium Concentration

Fig. 6.3 illustrates the ammonium concentration of the leachate from the HSWi reactor in comparison with the MSW reactor. The ammonium concentration is much lower in the HSWi reactor than in the MSW reactor, which indicates that there is no biodegradation of proteins inside the incineration ash landfill reactor.



Fig. 6.3 Ammonium Concentration of the leachate from HSWi and MSW Reactor

# Fatty Acids of the Leachate from HSWi Landfill Reactor

The investigation of fatty acids concentration of the leachate from HSWi reactor shows there is no fatty acids detected in this reactor, which once more proves there is no biodegradation inside the hospital waste incineration ash.

# 6.3 CO-DISPOSAL OF HOSPITAL WASTE INCINERATION ASH WITH MUNICIPAL SOLID WASTE

### 6.3.1 Waste Samples Characteristics

The municipal solid waste has the same composition as described in Table 5.1.

The dry weight of municipal solid waste (MSW) and hospital waste incineration ash (HSWi) is summarized in Table 6.2.

The waste was put in a 120 I landfill simulating reactor in the following way: the municipal solid waste and hospital waste incineration ash was put layer by layer as explained in Chapter 3.

Waste type	Dry weight (kg)
HSWi	42.963
MSW	6.280
Total	49.243

Table 6.2 Dry Weight of Waste Sameples

### 6.3.2 Hydraulics

The same rain ratio as in Chapter 5 was used as 3.6 l/(kg\*a). The waste was initially adjusted to 65% moisture content. Every 10 days, 4.8 I leachate was taken out for sampling and the same amount of new water was added in.

8-10 I of leachate was recycled every day.

# 6.3.3 Biodegradable Carbon Content

Hospital waste incineration ash does not contain biodegradable organics.

Use equation 4.2 for the calculation of biodegradable carbon content of municipal solid waste. Then for the mixture:

the dry weight of biodegradable carbon = 1.094 kg Biod. C

# 6.3.4 Maximum Gas Amount Prediction

The same procedures of calculation as Chapter 5.2.4 are carried out for the HSWi+MSW reactor.

Total theoretical amount of gas generated per unit of dry weight of MSW is 0.356 m<sup>3</sup>/kg dry waste.

The volume of gas amount generated from MSW is 0.356\*6.28=2.236m<sup>3</sup>

The incineration ash does not generate gas as tested in Chapter 6.2.

Therefore, the total theoretical gas amount for the mixture of hospital waste incineration ash and municipal solid waste is 2.236 m<sup>3</sup>.

### 6.3.5 Results and Discussions

# Gas Production

The accumulative gas amount of the mixture of hospital waste incineration ash and municipal solid waste (MSW+HSWi) reactor is shown in Fig. 6.4 in comparison with the pure municipal solid waste (MSW) reactor and the mixture of sterilized hospital waste and municipal solid waste (MSW+HSWs) reactor described in Chapter 5.

The gas production of the pure municipal solid waste (MSW) reactor and the mixture of sterilized hospital waste and municipal solid waste (MSW+HSWs) reactor is similar, respectively as 120 l/kg dry mass and 113 l/kg dry mass. But the gas production of the mixture of hospital waste incineration ash and municipal solid waste (MSW+HSWi) reactor is 505 l/kg dry mass. The gas production based on biodegradable carbon content is respectively 690 l/kg Biod.C, 1002 l/kg Biod.C and 2903 l/kg Biod.C in the MSW, MSW+HSWs and MSW+HSWi reactor.

This indicates the incineration ash has large effect on the biodegradation of municipal solid waste. It can enhance the gas production. The gas production is 4 times higher than that of the municipal solid waste. In addition, the gas amount even exceeded the maximum theoretical gas amount of 1867 I/kg biodegradable carbon. This means, the ash can also help to degrade some hardly degradable carbon and enhance the stabilization and reclamation of landfill site.





Fig. 6.4: Accumulative Gas Production

### Gas Composition

Fig. 6.5 illustrates the CH<sub>4</sub> and CO<sub>2</sub> development in the MSW+HSWi reactor.



Fig. 6.5: Gas Composition of the MSW+HSWi Reactor

Fig. 6.6 illustrates the CH<sub>4</sub> and CO<sub>2</sub> development in three reactors.

Methane starts to generate on 7th day in the MSW+HSWi reactor, while it appears only on 16th day in the MSW and MSW+HSWs reactor. Methane reaches 50% within 43 days in the MSW+HSWi reactor, while it needs 95 days to reach 50% of methane in the MSW and MSW+HSWs reactors. This means a shorter lag time in the mixture of incineration ash and municipal solid waste than in the pure municipal solid waste. The incineration ash can accelerate the methane production.

The CO<sub>2</sub> reaches higher concentration in the MSW reactor at first, followed by MSW+HSWs reactor and MSW+HSWi reactor. This may be due to the higher organic content for aerobic degradation in the MSW reactor than in case of the others.



Fig. 6.6: CH4 and CO2 Concentration Development

#### ● pH

Fig. 6.7 illustrates the pH value of the leachate from the MSW+HSWi reactor in comparison with the MSW and the MSW+HSWs reactor.

A low pH < 5.5 was reached on 7th day after waste placement in the MSW and MSW+HSWs landfill reactors as shown in Fig. 6.7. Under these conditions the fermentative and methanogenic bacteria are not able to develop. Later on, after growth of methanogenic bacteria and the conversion of organic acids to methane, pH gradually increases to 7.

However, the pH value in the MSW+HSWi reactor started with a higher value around 6.3

than the others. It keeps within the optimal range 6.5-7.0 for methanogenic bacteria during all the biodegradation process and gradually reaches 7.24.

The methanogenic bacteria are quite sensitive to changes in pH. It has been found <sup>[5]</sup> that the rate of methane fermentation is relatively constant within the pH range of 6.0 to 8.5, but drops very rapidly outside this range. Stegmann and Spendlin<sup>[19,20]</sup> reported that addition of Ca(OH)<sub>2</sub> or NaOH resulted in a shorter lag phase, but did not enhance the methane production. Other researchers came to the conclusion that addition of buffer may especially be helpful to overcome the inhibition of the acid producing bacteria<sup>[19]</sup>.

Incineration ash may not only shorten the lag phase but also enhance the methane production. Ash contains a high content of metal oxides and its salts. This reservoir of alkalinity first neutralizes the pH value to accelerate the acetogenesis process while the metal oxides are converted e.g. to carbonates and hydrogen carbonates. These compounds then act as a buffer system keeping pH within or close to the range which is optimal for methanogenic bacteria growth. As a result, methane starts early, and methane production is enhanced.



Fig. 6.7: PH Value of the Leachate

### Conductivity and Anion concentrations of leachate

Table 6.3 shows the conductivity and anion concentration of the leachate from the three reactors. It is much higher both in conductivity and in anion concentrations in the mixture of incineration ash and municipal solid waste reactor than in case of the other two. This shows that the cation and anion concentrations are much higher in the MSW+HSWi reactor.

It indicates that the cations from the incineration ash may affect the rate of methane formation. High content of cations may provide sufficient nutrients for bacteria growth and
thus promote the biodegradation process. However, because of the limit of financial resources, further investigation on the cation species and concentrations was not carried out yet.

The high content of sulphate might result in inhibition by substrate competition. However, the experimental results do not show inhibition. The reason might be in a higher pH condition, the sulphate-reducing bacteria is not as active as in an acid condition because some of the conversions need to consume  $H^+$  as shown in equation 2.5. It is not clear if the substrate is still enough for both sulphate reducing bacteria and methanogenic bacteria, because from the gas production it can be seen that easily biodegradable organics are consumed after 80 days and even other organics are fermented now. Another reason may be that at pH higher than 6  $H_2S$  starts to deprotonate which makes it less toxic for methanogenic bacteria.

	MSW	MSW+HSWs	MSW+HSWi
Conductivity(ms/cm)	10.2	10.4	24.8
Sulphate(mg/l)	400	400	2000
Chloride(mg/l)	200	300	4900

Table 6.3: Conductivity and Anion Concentration of Leachate

# • Fatty Acids

Table 6.4 shows the fatty acid concentrations on 10th day of each reactor.

The total fatty acids concentration on 10th day in the MSW+HSWi reactor is 4 times lower than in the MSW and MSW+HSWs reactor. This may indicate the methanogenic bacteria more effectively converted fatty acid to methane in the mixture of ash and municipal solid waste. The methanogenisis phase is not the limiting phase and hydrolysis may become the limiting step of biodegradation in this reactor.

In the MSW and MSW+HSWs reactors, butyric acid is the main kind of fatty acids. It indicates the conversion from butyric acid to propionic acid or acetic acid may be the limiting step of biodegradation in these two reactors.

The acetogenic step is thought to be the rate determining step of fermentation <sup>[21]</sup>. Enhancement of the acetogenisis process can also enhance the biodegradation process. Equation 6.1 shows the conversion from butyric acid to acetic acid.

$$CH_{3}(CH_{2})_{2}COO^{-} + 2H_{2}O \rightarrow 2CH_{3}COO^{-} + H^{+} + 2H_{2}$$
 (6.1)

Increasing the pH by alkalinity from ash can shift the equilibrium of equation 6.1 towards the acetic acid by removal of  $H^+$ , and thus stimulate the acetogenisis step.

Another aspect of the stimulation of acetogenisis may result from equation 6.2.

$$NAD^+ + H_2 \rightarrow NADH + H^+ \tag{6.2}$$

In equation 6.2, NAD<sup>+</sup>, NADH – nicotinamide adenine dinucleotide, is hydrogen transporting coenzyme needed for many metabolic processes.

By alkalinity from the ash, the equilibrium of equation 6.2 can be shifted towards the removal of  $H_2$ . By removal of  $H_2$ , the conversion of butyric acid and propionic acid to acetic acid could be stimulated.

	MSW(mg/l)	MSW+HSWs(mg/l)	MSW+HSWi(mg/l)
Acetic acid	107	80	24
Propionic acid	60	251	32
Butyric acid	336	243	61
Isovaleric acid	26	14	9
n-valeric acid	9	7	35
Caproic acid	4	26	2
Hexanoic acid	39	26	8
Nanoic acid	19	28	0.2
Total	720	847	170

Table 6.4: Fatty Acids Concentration on 10<sup>th</sup> day

# • COD and Ammonium-nitrogen

Fig. 6.8 illustrates the COD and Ammonium concentration in the three reactors. The COD concentration is lower in the MSW+HSWi reactor than in the other two reactors, which once more indicates the better conversion of organics into methane in the mixture of ash and municipal solid waste.



Fig. 6.8 COD and Ammonium Concentration

#### **6.4 DISCUSSION**

Enhancement of biological degradation processes in landfills can be achieved by accelerating the reaction rate of hydrolysis, acetogenisis and methanogenisis phases.

Hydrolysis is a very important process in the landfill environment. The rate limiting influence on enzymatic hydrolysis results from a combination of surface area effects and changes in crystallinity. Moisture has a distinct influence on the hydrolysis process of solid waste. Incineration ash provides high surface area and high water-hold ability, therefore it can accelerate the hydrolysis phase. Spendlin<sup>[20]</sup> used 1:1 mixture of high surface area clay in order to reach early methane production, but needs 170 days to reach 50% methane.

In the acetogenic stage, the high production of organic acids results in a low pH-value, and methanogenic bacteria are not able to develop. Stegmann<sup>[19]</sup> proposed it might be advantageous for the initial phase of methane production if there is a "dilution" effect where

the organic acids concentrations in the system become lower. This may be the case in the mixture of sterilized hospital waste and household waste. The lower biodegradable organic concentration in hospital waste may dilute the high organic content in household waste, and also enlarge the surface area for organic mass transport. But in the case of the mixture of incineration ash and household waste, the incineration ash not only can dilute the organic acids, but also neutralize the pH and thus accelerate the acetogenic stage.

The methane fermentation is generally assumed to be the rate-controlling step in anaerobic waste treatment process. The methane bacteria are quite sensitive to changes in pH. The presence of buffering material in the landfill will significantly improve the ability of landfill environment to maintain a reasonable pH range. The sufficient alkalinity of the incineration ash acts essentially as a buffer to the system for pH control instead of simply neutralization of the pH-value using NaOH or Ca(OH)2. Ash keeps the optimal pH-value for methanogenic bacteria growth.

In addition, the cation inside the incineration ash may affect the rate of methane formation and may also provide sufficient nutrients for anaerobic ecosystem.

# **Chapter 7 Kinetic Model of Gas Production Rate**

# 7.1 INTRODUCTION

The main problem of modeling biogas production is not only to forecast the amount of landfill gas which will be produced, but also the rate and the duration of the production. There are two main reasons for studying the rates of reactions. The first is the practical importance of being able to predict how quickly a reaction mixture approaches equilibrium. This rate might depend on variables under our control, such as pressure, temperature and presence of a catalyst, and we may be able to optimize it by the appropriate choice of conditions. The second reason is that the study of reaction rates leads to an understanding of mechanisms of the reactions, and to the analysis of a chemical reaction into a sequence of elementary steps.

Landfill gas (LFG) model is able to forecast the yield and production rate of biogas generated, or to evaluate the potential gas migration and related problems.

The static gas model has been presented in Chapter 4 for theoretical maximum gas production. This chapter presents a simplified deterministic gas production kinetic model which is valuable for practice. A complex deterministic biodegradation model which concerns variable parameters and mechanisms will be discussed in next chapter.

# 7.2 MODEL SELECTION

Depending on the approach, different classifications of models are possible:

A general classification can be based on the availability of data and the state of knowledge of the system:

- Statistical analysis, when a large number of data are available, but knowledge of the system is inadequate, and the data are collected for different purposes; this kind of model does not assume any cause-effect relation or deal with the temporal dynamics of the system, but presents the general characteristics of the data "population" and provides correlations.
- Stochastic model, which describes the temporal trend of data without explaining the same; this kind of model is useful for describing the behaviour of a black-box system, it states simply which is the output related to a specific input.
- Simplified deterministic model, which requires knowledge of the mechanisms governing the system; it is able to describe the behaviour of the system with simplified mathematical equations.
- Complex deterministic model, which acts in a similar way to the above-mentioned model using more complex mathematical equations.

The LFG models can be further divided into static and dynamic models. In static models there is an instantaneous relation between input and output, meaning that the system has no memory of the past input and output; the state of the system is stationary, there is no time influence. In dynamic models the relation between input and output is not instantaneous, and state variables that describe the temporal evolution of the system should be introduced.

Theoretically a complete biogas model should include three submodels:

- Stoichiometric submodel. This gives the maximum theoretical yield of biogas from the anaerobic degradation of the organic waste fraction. This model is static, which has been presented in Chapter 4 by maximum gas prediction.
- Kinetic submodel. This is a dynamic model, which gives as a result of the temporal evolution of LFG generation rates. It can be either an empirical model, based on a more or less simple equation of a defined order; or a deterministic model, based on a set of equations describing the degradation of the different biodegradable waste fractions; or an ecological model, which describes the dynamic of microbial populations and substrata within the landfill. This is the model which will be presented in this chapter.
- Diffusion submodel. This is a dynamic model, which describes the time and space variation of pressure and gas composition within the landfill body. LFG emission rates can be obtained, and the effectiveness of the gas extraction system can be verified. This model will be discussed in the next chapter.

In this chapter, a simplified deterministic kinetic model will be chosen to describe the degradation of waste. The model will be derived from mechanisms of chemical reaction rate, enzyme-catalysed reaction rate and micro-organism growth rate. The biodegradability of each waste fraction will be taken into concern using a term as biodegradable carbon content, whose calculation and determination method has been presented in Chapter 4.

#### 7.3 MODEL DERIVATION

#### 7.3.1 Rate Law of Reaction

For a reaction:

$$A + B \to C + D \tag{7.1}$$

The reaction rate dependent on concentration change of A is proportional to the concentrations of the reactants raised to some power

$$\frac{d[A]}{dt} = -k[A]^{m}[B]^{n}$$
(7.2)

Where: k= rate constant or rate coefficient, independent of the concentrations but dependent on the temperature.

m, n = order of with respect to some component.

The overall order of a reaction is the sum of the orders of all the components.

#### 7.3.2 Enzyme Reactions

The overall rate of biological reaction within a reactor depends on the catalytic activity of the enzymes in the prominent reaction. If it is assumed that enzyme-catalysed reactions involve the reversible combination of an enzyme (E) and substrate (S) in the form of a complex (ES) with the irreversible decomposition of the complex to a product (P) and the free enzyme (E), then the overall reaction can be expressed as:

$$E + S \xleftarrow[k_2]{k_1} ES \xrightarrow[k_3]{k_3} E + P$$
(7.3)

Where  $k_1$ ,  $k_2$ , and  $k_3$  represent the rate of the reactions. Under steady-state ( $C_{ES}$  = constant) conditions the various rate constants can be expressed as:

$$\frac{(k_2 + k_3)}{k_1} = k_m \tag{7.4}$$

where  $k_m$  is the saturation or Michaelis constant. The Michaelis-Menten equation allows the reaction rate of enzyme-catalysed reactions to be calculated:

$$r = \frac{R_{\max} * C}{K_m + C} \tag{7.5}$$

where r is the reaction rate,  $R_{max}$  is the maximum rate at which the product is formed, and C is the substrate concentration.

At low substrate concentrations,  $K_m + C \approx K_m$ , the rate of enzyme-catalysed reaction is proportional to the substrate concentration (first-order). At high substrate concentrations,  $K_m + C \approx C$  the rate of reaction becomes constant and independent of substrate concentration (zero-order).

In practical terms, this is seen when a batch reactor is started and no further substrate is added. Initially, the rate of reaction is only restricted by the ability of the enzymes to utilize the substrate which is in excess, thus the reaction kinetics are zero-order. However, as the substrate is utilized the reaction begins to become substrate-limited resulting in fractional-order reactions until the substrate concentration is so low that the rate of reaction becomes totally limited by the substrate concentration, and thus first-order kinetics result.

#### 7.3.3 Kinetic Equation of Bacterial Growth

The most commonly used model, relating microbial growth to substrate utilization, is

Monod Equation.

$$\mu = \mu_{\rm m} \frac{C}{k_s + C} \tag{7.6}$$

This equation describes the relationship between the residual concentration of the growth limiting substrate or nutrient, and the specific growth rate of biomass ( $\mu_m$ ) is the maximum specific growth rate at saturation concentration of growth limiting substrate, and  $k_s$  is the saturation constant, which is the concentration of limiting substrate at which the specific growth rate equals one-half of the maximum specific growth rate.

This equation describes that the overall rate of metabolism is controlled by the substrate concentration. The Monod relationship has the same form as the Michaelis-Menten equation. The microbial growth rate increases as the availability of substrate increases until the maximum specific growth rate is achieved, at which point a factor other than substrate, such as generation rate or a specific nutrient, becomes growth-limiting.

For a long retention time biological reactor, the basic equation for microbial growth can be expressed in the following equation:

$$\frac{dX}{dt} = (\mu - \mathbf{k}_{d})\mathbf{X}$$
(7.7)

where kd is the specific endogenous decay rate which includes endogenous respiration, death, and subsequent lysis; X is the microbial concentration.

The mass of organisms produced is related to the mass of substrate consumed, using the expression:

$$\frac{dX}{dt} = -Y\frac{dC}{dt}$$
(7.8)

where Y is the yield coefficient.

#### 7.3.4 Rate of Biogas Production

The overall methane fermentation process for organics in solid waste can be represented by the following equation:

$$C_aH_bO_cN_d + nH_2O \rightarrow xCH_4 + yCO_2 + wNH_3 + zC_5H_7O_2N + energy$$
(7.9)

The general equation of the rate of biogas production dependent on substrate concentration is:

$$\frac{dC}{dt} = -kC^n = f(t, C^n)$$
(7.10)

where: C= the amount of biodegradable organics

t= time

Equation 7.10 can express either the rate of substrate degradation or the rate of gas

production. It is applied to a single batch of waste, which often corresponds to the amount of waste disposed either in a single layer or in a year. As a consequence, LFG models can apply to each waste batch independently. The global LFG production rate is given by the sum of the single batch contributions.

The greatest absolute exponent n of the dependent variable is called the order of the model.

A zero-order kinetic means that a small increment (positive or negative) of C does not influence the rate of substrate decay or biogas production. In other words, a zero-order model indicates that the rate of methane generation is independent of the amount of substrate remaining or of the amount of biogas already produced. Many landfills have a biogas production that follows a zero-order kinetics, especially during the periods of highly active gas generation: probably other factors such as moisture, nutrients etc., limit the amount of methane to be formed, resulting in a relatively constant gas production independent of time.

The majority of LFG production models follow a first-order kinetics, which means that the limiting factor is the remaining amount of substrate or the amount of biogas already produced. In this way, other factors such as moisture or nutrient availability are not supposed to be limiting factors. Actually, in many cases the limiting factor is the water content, which plays a major role in the hydrolysis of organic matter. Although it is clear that many factors such as moisture, temperature, availability of nutrients and presence of the necessary micro-organism influence the biogas production, most authors believe that a first-order kinetic with respect to substrate is the most suitable. This choice appears to be supported by the fact that the gas production gradually declines in the long term.

#### 7.3.5 Model Determination

In a landfill batch reactor, the following assumptions can be drawn:

1, initial substrate concentration is  $C_0$ , no more substrate is added.

2, long retention time reactor

For a given species of micro-organism and given substrate, the biological reaction rate should follow Michaelis-Menten equation.

$$r = \frac{dC}{dt} = \frac{R_{\max} * C}{K_m + C}$$
(7.11)

In the initial period after waste placement, the rate of reaction can be assumed to be restricted by the ability of the enzymes to utilize the substrate which is in excess, thus the reaction kinetics are zero-order:

$$\frac{dC}{dt} \approx \mathsf{R}_{\mathsf{max}} \tag{7.12}$$

Under landfill conditions again substrate limitation is observed as explained in Chapter 7.3.2. That means that at low substrate concentration, first-order kinetics result:

$$\frac{dC}{dt} \approx \frac{R_{\text{max}}}{K_m} C$$
(7.13)

Landfill gas production rate not only depends on enzyme reaction rate, but also depends on micro-organisms growth rate because enzyme is produced by micro-organisms. Rearrange equation 7.8:

$$\frac{dC}{dt} = -\frac{1}{Y}\frac{dX}{dt}$$
(7.14)

Cite equation 7.7 into equation 7.14:

$$\frac{dC}{dt} = -\frac{1}{Y}(\mu - k_d)X$$
(7.15)

Cite equation 7.6 into equation 7.14:

$$\frac{dC}{dt} = -\frac{1}{Y} (\mu_{\max} \bullet \frac{C}{K_s + C} - k_d) X$$
(7.16)

In initial period of waste placement, substrate concentration is high. Equation 7.16 can be written as following:

$$\frac{dC}{dt} = -\frac{1}{Y}(\mu_{\max} - k_d)X$$
(7.17)

At low substrate concentration,  $K_s + C \approx K_s$ , equation 7.16 can be written as following:

$$\frac{dC}{dt} = -\frac{1}{Y} \left(\frac{\mu_{\text{max}}}{K_s} \bullet C - k_d\right) X$$
(7.18)

For a given species of micro-organism, Y,  $\mu_{max}$ ,  $k_d$ ,  $K_s$  are constants. If we assume, in optimal landfill conditions, the micro-organism concentration X does not change during the whole landfill biodegradation process and  $k_d$  can be neglected, the equation 8.17 and 8.18 can be simplied as following:

$$\frac{dC}{dt} = -k_1 \quad \text{(high substrate concentration)}$$
$$\frac{dC}{dt} = -k_2C \quad \text{(low substrate concentration)}$$

Under landfill conditions, different species of micro-organisms consume different species of substrates. The total reaction rate could be the sum of all waste components.

$$\frac{dC}{dt} = \sum \frac{dC_i}{dt}$$
(7.19)

#### 7.3.6 Model Discussion

Under landfill conditions, it is difficult to verify the species of micro-organisms. For practical use, only the overall amount of biodegraded organic waste is meaningful. Therefore, this model takes account of different biodegradability of each waste fraction by using a general term: biodegradable carbon content, whose calculation and determination method has been described in Chapter 4. By this way the substrate concentration is expressed by a general term: g biodegradable carbon per kg dry waste. Thus complicated computerization of each waste fraction is avoided.

Based on the above derivation of enzyme reaction rate and micro-organism growth rate, a two-stage model combining zero-order and first-order kinetics is proposed here.

$$\frac{dC}{dt} = -k_1, (t = [0, p])$$

$$\frac{dC}{dt} = -k_2C, (t = [p, t])$$
(7.20)

Where: C = substrate concentration

t = time

 $k_1, k_2, p = constants$ 

This model combines the advantages of zero-order kinetic model and first-order kinetic model. It can simulate the actual landfill process more precisely and explain in a better way the interaction of different factors under landfill conditions.

In the first period, from waste placement until the peak value of gas production is finished, the amount of substrate is not the limiting factor for biodegradation because we can propose substrate is sufficient for all type of bacteria. Therefore, other factors such as pH, moisture, nutrients, temperature, surface area etc. become the limiting factors for gas production rate. These factors may affect the lag time and the period to reach the peak value of gas production on the one hand, on the other hand they may affect the total gas amount.

In the second period, when substrate is not sufficient for all bacteria, substrate concentration becomes the limiting factor. Under this condition, bacteria compete for substrate. Those bacteria who consume less energy will dominate the biodegradation process. In this case, the bacteria responsible for hydrolysis, acetogenisis and methanogenis need to coordinate and form an optimal combination for this ecosystem.

The assumption for this model is that the micro-organism concentration during all biodegradation process does not change. However, actually the micro-organisms concentration is not always constant. Especially initially there is a short period for bacteria growth after waste placement. In this period, the error of the model for actual landfill gas

production rate may become bigger because the constant micro-organism concentration assumption is not the true situation. However, compared with the whole biodegradation process, the error from this short period has no big effect on the gas prediction for the long term.

#### 7.3.7 Mathematic Solution of the Kinetic Model

The solution for equation 7.19 is shown in following: Rearrange the zero-order equation as the following:

$$dC = -k_1 dt \tag{7.21}$$

Integrate this differential equation:

$$\int dC = \int -k_1 dt \tag{7.22}$$

Initially (at t=0) the concentration of substrate is  $C_{01}$ , and the later time is  $C_t$ . The solution can be expressed in following form:

$$C_t = C_{01} - k_1 t + m_1 \tag{7.23}$$

Where  $m_1$  = integrating constant.

Initially when t=0,  $C_t=C_{01}$ , so:

Then equation 7.22 becomes:

$$C_t = C_{01} - k_1 t \tag{7.24}$$

The first-order differential equation rearranges to:

$$\frac{dC}{C} = -k_2 dt \tag{7.25}$$

which can be integrated:

$$\int \frac{dC}{C} = -\int k_2 dt \tag{7.26}$$

$$\ln C_t - \ln C_{02} = -k_2 t + k_2 p + m_2 \tag{7.27}$$

Where  $m_2$  = integrating constant.

When t=p,  $C_t=C_{02}$ . Then:

$$m_2 = 0$$

Then equation 7.26 can be expressed as:

$$\ln C_t / C_{02} = -k_2 t + k_2 p$$

$$C_t = C_{02} e^{-k_2(t-p)}$$
(7.28)
(7.29)

Therefore, combining with equation 7.23 and equation 7.28, the solution of the kinetic model is:

$$C_{t} = C_{01} - k_{1}t, t = [0, p]$$

$$C_{t} = C_{02}e^{-k_{2}(t-P)}, t = (p, t]$$
1 mol C = 22.4 | biogas at STP
1 q C = 1.867 | biogas

So the accumulative gas production:

$$G=-1.867(C_t-C_{01})$$
(7.31)

Use equation 7.31 to equation 7.30:

$$G = 1.867k_{1}t, t = [0, p]$$

$$G = 1.867C_{01} - 1.867C_{02}e^{-k_{2}(t-P)}, t = (p, t]$$
(7.32)

Gas production rate can be got from equation 7.32:

$$\frac{dG}{dt} = 1.867k_1, t = [0, p]$$

$$\frac{dG}{dt} = 1.867C_{02}k_2e^{-k_2(t-p)}, t = (p, t]$$
(7.33)

#### 7.3.8 Parameters Definition of the Kinetic Model

Table 7.1 summarizes the parameters definition of the kinetic model.

Notation	Unit	Definition
t	day	Time
Ct	g Biod.C/kg dry waste	Substrate concentration at time t
р	day	Time of peak value of gas production
<b>k</b> <sub>1</sub>	g Biod.C/(kg dry waste*day)	Rate constant
<b>k</b> <sub>2</sub>	1/day	Rate constant
C <sub>01</sub>	g Biod.C/kg dry waste	Substrate concentration at time t=0
C <sub>02</sub>	g Biod.C/kg dry waste	Substrate concentration at time t=p, C <sub>02</sub> =
		C <sub>01</sub> - k <sub>1</sub> p

Table 7.1: Parameters Definition of Kinetic Model

# 7.4 GAS PRODUCTION RATE KINETIC MODEL FOR MUNICIPAL SOLID WASTE WITH LEACHATE RECYCLING

Apply the above kinetic model to the pure municipal solid waste (MSW) landfill reactor with leachate recycling which was described in Chapter 5.

The initial substrate concentration:

C<sub>01</sub> = 174 g Biod.C/kg dry waste

Fig. 7.1 shows the experimental accumulative gas production development with time.

Fig. 7.2 shows the experimental substrate concentration development with time.

Fig. 7.3 shows the experimental gas production rate development with time.

From the figures it can be clearly seen that the time of peak value of gas production:



p = 80 d

Fig. 7.1: Accumulative Gas Production of MSW Reactor with Leachate Recycling



Fig 7.2: Substrate Concentration of MSW Reactor with Leachate Recycling



Fig. 7.3: Gas Production Rate of MSW Reactor with Leachate Recycling

From 0-80 days, from equation 7.30 and Fig. 7.2, the rate constant  $k_1$  can be achieved:  $k_1 = 0.5208$  g Biod.C/ (kg dry waste\*day)

From 80-150 days, the rate constant k<sub>2</sub> can be achieved:

$$k_2 = 0.0018 \text{ day}^{-1}$$

So,

$$C_{02} = C_{01} \cdot k_1 p = 132 g Biod.C/kg dry waste$$

Then the kinetic model for MSW reactor with leachate recycling is expressed in following:

$$C_{t} = 174 - 0.5208t, t = [0,80]$$

$$C_{t} = 132e^{-0.0018(t-80)}, t = [80, t]$$
(7.34)

The accumulative gas production kinetic model can be got out from equation 7.32 and is shown in the following:

$$G = 0.9723t, t = [0,80]$$
  

$$G = 325 - 246e^{-0.0018(t-80)}, t = [80,t]$$
(7.35)

Gas production rate can be derived from equation 7.33:

$$\frac{dG}{dt} = 0.9723, t = [0,80]$$

$$\frac{dG}{dt} = 0.4428e^{-0.0018(t-80)}, t = (80,t]$$
(7.36)

Fig. 7.4 illustrates the comparison with model data and experimental data.

It can be seen that model data fits to experimental data very well on substrate concentration and accumulative gas product. But for the instantaneous gas production rate of the initial period, model data do not fit to the experimental data. The reason might be the fluctuant bacteria concentration in the laboratory landfill reactor. (Cf. Chapter 7.3.6)

The biggest relative error for substrate concentration between model data and experimental data is 7.3%.

The biggest relative error for accumulative gas production between model data and experimental data is 10.0%.

The biggest error for instantaneous gas production rate between model data and experimental data is 47.4%







Fig. 7.4: Model Data Versus Experimental Data

The kinetic models of other reactors are carried out in the same way and attached in the appendix.

# 7.5 DISCUSSION

Table 7.2 summarizes modeling results.

Reactor	Result	Constants
MSW reactor	$C_t = 174 - 0.5208t, t = [0,80]$	k <sub>1</sub> = 0.5208 g Biod.C/ (kg dry
with leachate	$C_t = 132e^{-0.0018(t-80)}, t = [80, t]$	waste*day)
recycling	G = 0.9723t, t = [0,80]	$k_2 = 0.0018 \text{ day}^{-1}$
	$G = 325 - 246e^{-0.0018(t-80)}, t = [80, t]$	$C_{01}$ = 174 g Biod.C/kg dry waste
	dG a grad to again	C <sub>02</sub> = 132 g Biod.C/ kg dry waste
	$\frac{1}{dt} = 0.9723, t = [0,80]$	
	$\frac{dG}{dt} = 0.4428e^{-0.0018(t-80)}, t = (80, t]$	
MSW+HSWs	$C_t = 114 - 0.4687t, t = [0,80]$	k <sub>1</sub> = 0.4687 g Biod.C/ (kg dry
reactor with	$C_t = 76.5e^{-0.0038(t-80)}, t = [80, t]$	waste*day)
leachate	G = 0.8751t, t = [0,80]	k <sub>2</sub> = 0.0038 day <sup>-1</sup>
recycling	$G = 213 - 143e^{-0.0038(t-80)}, t = [80, t]$	C <sub>01</sub> = 114 g Biod.C/kg dry waste

	$\frac{dG}{dt} = 0.8751, t = [0,80]$ $\frac{dG}{dt} = 0.5427e^{-0.0038(t-80)}, t = (80,t]$	C <sub>02</sub> = 76.5 g Biod.C/ kg dry waste
MSW+HSWi	$C_t = 174 - 2.7991t, t = [0,80]$	k <sub>1</sub> = 2.7991 g Biod.C/ (kg dry
reactor with	$C_t = 50e^{-0.0355(t-80)} - 100, t = [80, t]$	waste*day)
lechate	G = 5.2259t, t = [0,80]	$k_2 = 0.0355 \text{ day}^{-1}$
recycling	$G = 511.6 - 93.4e^{-0.0355(t-80)}, t = [80, t]$	$C_{01}$ = 174 g Biod.C/kg dry waste
	$\frac{dG}{dt} = 5.2259, t = [0,80]$ $\frac{dG}{dt} = 3.3139e^{-0.0355(t-80)}, t = (80,t]$	C <sub>02</sub> = -50 g Biod.C/ kg dry waste
MSW reactor	$C_t = 105 - 0.0255t$	k <sub>1</sub> = 0.0255 g Biod.C/ (kg dry
without	G = 0.0476t	waste*day)
leachate recycling *	$\frac{dG}{dt} = 0.0476$	$C_{01}$ = 174 g Biod.C/kg dry waste
HSWs	$C_t = 42 - 0.0098t$	k <sub>1</sub> = 0.0098 g Biod.C/ (kg dry
reactor	G = 0.0183t	waste*day)
without	dG o o log	$C_{01}$ = 42 g Biod.C/kg dry waste
leachate	$\frac{dt}{dt} = 0.0183$	
recycling *		

Table 7.2: Gas Production Kinetic Modeling Results

\* Reactor does not reach the second period of substrate limitation

Comparing the rate constants for these 5 reactors, it can be clearly seen that the rate constant for the mixture of hospital waste incineration ash and municipal solid waste is one order of magnitude higher than municipal solid waste with leachate recycling, two orders of magnitude higher than municipal solid waste without leachate recycling.

Comparing the rate constants for municipal solid waste with leachate recycling and without leachate recycling, it can be concluded that leachate recycling can promote one order of magnitude higher biodegradation rate than that without leachate recycling.

Comparing the rate constants for municipal solid waste and the mixture of sterilized hospital waste and municipal solid waste, the rate constants are in the same order of magnitude. It can be concluded that co-disposal of sterilized hospital waste does not significantly affect the biodegradation of municipal solid waste landfill site.

Comparing the rate constants for sterilized hospital waste and the mixture of sterilized hospital waste and municipal solid waste, the rate constant for co-disposal of sterilized hospital waste with municipal solid waste is two orders of magnitude higher than the rate constant of pure sterilized hospital waste. It can be concluded that co-disposal of sterilized hospital waste is more advantageous for bio-gas production than separate disposal of sterilized hospital waste.

# Chapter 8 Diffusion Model for Biodegradation of Hospital Waste and Municipal Solid Waste

#### **8.1 INTRODUCTION**

The decomposition of solid waste is a complex and often unpredictable process. However, successful prediction is required if we want to improve environmental management of solid waste residues. Due to the intricate interaction between biology, chemistry and physics, a holistic approach to prediction would necessitate the inclusion of all three of these disciplines in an interrelated model.

This chapter presents a model of biodegradation processes for solid waste refuse. The model takes into account three key processes – hydrolysis, acidogenesis and methanogenesis – for waste decomposition. The model involves numbers of variable affecting factors for waste biodegradation process. In this model moisture content and flow parameters are input data. Simulation results can show the impact of numbers of affecting factors on key variables such as volatile fatty acid concentration, methanogenic biomass, and particularly on depletion of the solid organic fraction.

### 8.2 FICK'S LAW

The fundamental equation (one-dimensional) of molecular diffusion, known as Fick's first law, can be written for a binary mixture as

$$J_{A} = -\rho D_{AB} \frac{\partial \omega_{A}}{\partial x}$$
(8.1)

Where J<sub>A</sub>= mass flux of molecular species A relative to mass average velocity of the mixture, kg/m\*s

 $\rho = \rho_A + \rho_B$ , mass density (concentration) of the mixture, kg/m<sup>3</sup>

D<sub>AB</sub>= mass diffusivity of species A with respect to species B, m<sup>2</sup>/s

 $\omega$  A=  $\rho_A / \rho$  , mass fraction, kg/kg

### 8.3 DIFFERENTIAL FORM OF THE MASS-DIFFUSION EQUATION

Consider the conservation of species A in the element of volume  $\triangle x \triangle y \triangle z$  shown in Fig 8.1.



Fig 8.1: Differential Volume Element

Applying the conservation principle to the volume element gives:

Rate at which species A enters + rate at which species A is produced = rate at which species A leaves + rate at which species A accumulates (8.2)

Species A accumulates at the rate of

$$\frac{\partial \rho_A}{\partial t} \Delta x \Delta y \Delta z$$

The mass rate of A produced is

$$r_A \Delta x \Delta y \Delta z$$

where r<sub>A</sub> is the mass of A produced per unit volume per unit time.

Using these terms and fluxes in equation 8.2, we get:

$$N_{A}|_{x}\Delta y\Delta z + N_{A}|_{y}\Delta x\Delta z + N_{A}|_{z}\Delta x\Delta y + r_{A}\Delta x\Delta y\Delta z = N_{A}|_{x+\Delta x}\Delta y\Delta z + N_{A}|_{y+\Delta y}\Delta x\Delta y + N_{A}|_{z+\Delta z}\Delta x\Delta y + \frac{\partial\rho_{A}}{\partial t}\Delta x\Delta y\Delta z$$
(8.3)

Then we can get:

$$\frac{\partial N_{Ax}}{\partial x} + \frac{\partial N_{Ay}}{\partial y} + \frac{\partial N_{Az}}{\partial z} + \frac{\partial \rho_A}{\partial t} - r_A = 0$$
(8.4)

where  $N_A$  is the mass flux of species A.

# **8.4 BIODEGRADATION MODEL**

# 8.4.1 Model Derivation

The following aspects of this biodegradation process are taken into account in this model:

1, the molecular diffusion between solid waste particles and aqueous phase

- 2, the mass transfer by convection
- 3, bio-chemical reactions inside the aqueous phase

This model is based on the following assumptions:

1, the waste is homogeneous, there is no concentration gradient in the horizontal direction of landfill reactor. Only the concentration gradient in vertical direction is taking into account in this model.

2, it is assumed that the concentration distribution is such that the changes in density are small in relation to the density itself. This enables the density to be regarded as constant when it is not introduced as a difference.



Fig 8.2: Volume Element in Landfill

Consider the conservation of species A in the element of volume  $\triangle x \triangle y \triangle z$  shown in Fig 8.2.

$$N_{A}|_{x}\Delta y\Delta z + N_{A}|_{y}\Delta x\Delta z + N_{A}|_{z}\Delta x\Delta y + u\rho_{A}\Delta x\Delta y + r_{A}\Delta x\Delta y\Delta z =$$

$$N_{A}|_{x+\Delta x}\Delta y\Delta z + N_{A}|_{x+\Delta x}\Delta x\Delta z + N_{A}|_{y+\Delta y}\Delta x\Delta y + u(\rho_{A} + \frac{\partial\rho_{A}}{\partial z}\Delta z)\Delta x\Delta y + \frac{\partial\rho_{A}}{\partial t}\Delta x\Delta y\Delta z$$
(8.5)

Dividing by  $\triangle x \triangle y \triangle z$  and taking the limit as  $\triangle x$ ,  $\triangle y$ , and  $\triangle z$  approach zero, we get:

$$\frac{\partial N_{Ax}}{\partial x} + \frac{\partial N_{Ay}}{\partial y} + \frac{\partial N_{Az}}{\partial z} + u \frac{\partial \rho_A}{\partial z} + \frac{\partial \rho_A}{\partial t} - r_A = 0$$
(8.6)

Equation 8.6 can be simplified to one dimension:

227

$$\frac{\partial N_{Az}}{\partial z} + u \frac{\partial \rho_A}{\partial z} + \frac{\partial \rho_A}{\partial t} - r_A = 0$$
(8.7)

Use Fick's law:

$$N_{Az} = J_{Az} = -\rho D_{AB} \frac{\partial \omega_A}{\partial z}$$
(8.8)

Then we can get:

$$D_{AB}\frac{\partial^2 \omega_A}{\partial z^2} - u\frac{\partial \omega_A}{\partial z} + \frac{r_A}{\rho} = \frac{\partial \omega_A}{\partial t}$$
(8.9)

This equation is valid for mass conservation of both fatty acids and methanogenic biomass since fatty acids is converted directly to methanogenic biomass. These two processes use the same functional description – conventional Michaelis-Menten kinetics, with a yield parameter to control the relative masses of the two entities.

$$\frac{dM}{dt} = -Y\frac{dC}{dt}$$
(8.10)

where M is mass concentration of the methanogenic biomass in aqueous phase, C is the fatty acids concentration in aqueous phase, Y is the yield coefficient.

For the fatty acids concentration in the aqueous phase, equation 8.9 can be written as:

$$D_C \frac{\partial^2 C}{\partial z^2} - u \frac{\partial C}{\partial z} + r_C = \frac{\partial C}{\partial t}$$
(8.11)

For the methanogenic biomass in the aqueous phase, equation 8.9 can be written as:

$$D_{M} \frac{\partial^{2} M}{\partial z^{2}} - u \frac{\partial M}{\partial z} + r_{M} = \frac{\partial M}{\partial t}$$
(8.12)

#### 8.4.2 Fatty Acids Accumulation Rate Model

The fatty acids concentration in the aqueous phase depends not only on the molecular diffusion between solid waste particles and aqueous phase and the mass transfer between solid waste and falling liquid film, but also depends on the biochemical reaction rate of the hydrolysis stage and methanogenisis stage.

#### 8.4.2.1 Modeling of Fatty Acids from Hydrolysis Stage

In order to model the conversion from organic material in the solid phase to fatty acids in the liquid phase, the following parameters are captured in:

Maximum hydrolysis rate

This is the maximum or initial rate of hydrolysis of solid organic matter occurring under the most favourable substrate structure and interaction conditions. Cecchi <sup>[22]</sup> and Wang & Banks <sup>[23]</sup> indicate maximum volatile solid reduction rates in the range 4000 g to 5000g total volatile solid per m<sup>3</sup> solution per day. Estimates of maximum hydrolysis rate can also be made from fatty acids growth vs. time plots, e. g. from Barlaz <sup>[24]</sup>, a fatty acids growth rate of about 1800 mg/L solution/day.

• Relative Digestibility and Structural Transformation Parameter.

The presence of highly degradable organic matter and /or the initial colonisation and enzymati attack of exposed waste surfaces means that initial hydrolysis rates are rapid. Remaining organic matter, having become less accessible to, or shielded from, enzymatic attack, or with an increased crystallinity, becomes less digestible and is hydrolysed at slower rates. Lee & Fan <sup>[4]</sup> suggested that a lumped parameter, referred to as the relative digestibility, be used to reflect the combined effects of changes in accessible surface area and crystallinity. They found relative digestibility,  $\Phi$ , to be related to the extent of substrate conversion by a single parameter, n, the structural transformation parameter,

$$\phi = 1 - \left[\frac{S_0 - S}{S_0}\right]^n \tag{8.13}$$

Where S is the solid organic fraction remaining and  $S_0$  is the initial organic fraction.

Lee & Fan reported a value of 0.36 for the structural transformation parameter but indicated that it is probably strongly dependent on the structural features of the cellulose. In their tests, "Solka-Floc", a commercially available delignified cellulose was used, but lignin, a substance which is resisant to enzymatic hydrolysis and can shield cellulose, comprises up to 15% by dry weight of the organic fraction of waste refuse <sup>[25]</sup>. Calculations performed on data presented by Wald <sup>[26]</sup> for rice straw, a lignified cellulose, reveal a higher value (0.7) for the structural transformation parameter.

# Product Inhibition

To simulate reductions in enzyme-substrate activity due to product inhibition, a function P, based on a form defined by Lee & Fan<sup>[4]</sup> has been adopted,

$$P = \exp(-k_{FA}(C)) \tag{8.14}$$

Where  $k_{FA}$  is a product inhibition factor. Selection of a  $k_{FA}$  value is based on the maximum fatty acids concentration at which biodegradation is inhibited.

Combining the relative digestibility and product inhibition factor with an initial hydrolysis rate b, the enzymatic hydrolysis or fatty acids function r<sub>g</sub> can be expressed as:

$$r_g = b\phi P = b \left[ 1 - \left( \frac{S_0 - S}{S_0} \right)^n \right] \exp(-k_{FA}(C))$$
 (8.15)

#### Moisture Content Effects.

There is widespread agreement that one of the most important factors, and one that can be controlled most easily during the life of a landfill, is moisture content. Whilst the decay of fatty acids and the growth/decay of methanogic biomass are assumed to occur within the bulk aqueous phase, hydrolysis of solid organics is a surface phenomenon occurring at the interface between the aqueous and solid phases.

To control the influence of moisture on these surface processes, an effective moisture content term, which acts directly on the enzymatic hydrolysis/fatty acids growth function, has been introduced<sup>[27]</sup>. It is defined as:

$$\theta_E = \frac{\theta - \theta_R}{\theta_s - \theta_R} \tag{8.16}$$

Where  $\theta$  is volumetric moisture content, and subscripts E, S, R refer to effective, saturated and residual respectively.

Combining equation 8.15 and 8.16 gives an equation describing the enzymatic hydrolysis function  $r_H$  of waste refuse under a range of moisture contents:

$$r_{H} = \theta_{E} r_{g} = \theta_{E} b \phi P = \theta_{E} b \left[ 1 - \left( \frac{S_{0} - S}{S_{0}} \right)^{n} \right] \exp(-k_{FA}(C))$$
(8.17)

#### 8.4.2.2 Rate of Fatty Acids Depletion

The rate of fatty acids depletion  $r_d$  is directly related to methanogenic biomass accumulation.

$$r_d = \frac{r_{mg}}{Y} \tag{8.18}$$

Where Y is the yield coefficient.

The methanogenic biomass growth rate r<sub>mg</sub> is described by Monod kinetics:

$$r_{mg} = \frac{\mu_m C}{k_s + C} M \tag{8.19}$$

Where  $\mu_m$  is the maximum growth rate, and k<sub>s</sub> is the half saturation constant, and M is the methanogenic biomass concentration.

Cite equation 8.19 into equation 8.18, we get:

$$r_d = \frac{\mu_m C}{k_s + C} \frac{M}{Y}$$
(8.20)

#### 8.4.2.3 Fatty Acids Accumulation Rate Model

Combining equation 8.20 and equation 8.17, the fatty acids accumulation rate can be achieved:

$$r_{C} = r_{H} - r_{d} = \theta_{E} b \left[ 1 - \left( \frac{S_{0} - S}{S_{0}} \right)^{n} \right] \exp(-k_{FA}(C)) - \frac{\mu_{m}C}{k_{s} + C} \frac{M}{Y}$$
(8.21)

Coupling equation 8.21 with equation 8.11, the fatty acids concentration model can be achieved:

$$D_C \frac{\partial^2 C}{\partial z^2} - u \frac{\partial C}{\partial z} + \theta_E b \left[ 1 - \left( \frac{S_0 - S}{S_0} \right)^n \right] \exp(-k_{FA}(C)) - \frac{\mu_m C}{k_s + C} \frac{M}{Y} = \frac{\partial C}{\partial t}$$
(8.22)

#### 8.4.3 Methanogenic Biomass Accumulation Model

The methanogen growth rate  $r_{mg}$  is described by equation 8.19.

The methanogen decay rate  $r_{md}$  is given as:

$$r_{md} = k_d M \tag{8.23}$$

Where kd is the methanogen death rate coefficient.

Then methanogenic biomass accumulation rate is:

$$r_{M} = r_{mg} - r_{md} = \frac{\mu_{m}C}{k_{s} + C}M - k_{d}M$$
(8.24)

Methanogenic biomass accumulation model could be given as following:

$$D_M \frac{\partial^2 M}{\partial z^2} - u \frac{\partial M}{\partial z} + \frac{\mu_m C}{k_s + C} M - k_d M = \frac{\partial M}{\partial t}$$
(8.25)

#### 8.4.4 Complete Biodegradation Model

Substrate depletion rate r<sub>s</sub> is given as:

$$r_{s} = \frac{dS}{dt} = r_{H} = \theta_{E} b \left[ 1 - \left( \frac{S_{0} - S}{S_{0}} \right)^{n} \right] \exp(-k_{FA}(C))$$
(8.26)

Combining equation 8.22, equation 8.25 and equation 8.26, the complete biodegradation model can be given as:

$$D_{C} \frac{\partial^{2} C}{\partial z^{2}} - u \frac{\partial C}{\partial z} + \frac{\theta - \theta_{R}}{\theta_{s} - \theta_{R}} b \left[ 1 - \left( \frac{S_{0} - S}{S_{0}} \right)^{n} \right] \exp(-k_{FA}(C)) - \frac{\mu_{m}C}{k_{s} + C} \frac{M}{Y} = \frac{\partial C}{\partial t}$$

$$D_{M} \frac{\partial^{2} M}{\partial z^{2}} - u \frac{\partial M}{\partial z} + \frac{\mu_{m}C}{k_{s} + C} M - k_{d} M = \frac{\partial M}{\partial t}$$

$$\frac{dS}{dt} = \frac{\theta - \theta_{R}}{\theta_{R} - \theta_{s}} b \left[ 1 - \left( \frac{S_{0} - S}{S_{0}} \right)^{n} \right] \exp(-k_{FA}(C))$$
(8.27c)

This model combines mass transport terms and biochemical reaction rate. It concerns the mass transfer resulting from molecular diffusion and moisture flow, the affecting factors on hydrolysis, acidogenisis and methanogenisis processes, and the intricate relation between the different stages of waste biodegradation process.

The resulting biodegradation model requires 9 physical parameters, 3 initial conditions of variables and input data from hydraulic model. Tabel 8.1 summarizes the definition of parameters required for this model.

type	notation	definition
Transport	Dc	Diffusion coefficient of fatty acid
	D <sub>M</sub>	Diffusion coefficient of methanogenic biomass
Growth/decay	b	Hydrolysis rate
	n	Structural transformation
	k <sub>FA</sub>	Product inhibition
	μ <sub>m</sub>	Specific growth rate
	ks	Half-saturation constant
	k <sub>d</sub>	Methanogen death rate
	Y	Yield coefficent
Hydraulic data	u	Moisture flow rate
	θ	Moisture content
	$\theta_{R}$	Residual moisture content

	$\theta_{\rm s}$	Saturated moisture content
varible	С	Fatty acids concentration
	М	Methanogenic biomass
	S	Solid organic fraction
Initial conditions	C <sub>0</sub>	Initial fatty acids concentration
	M <sub>0</sub>	Initial methanogenic biomass
	S <sub>0</sub>	Initial solid organic fraction

Tabel 8.1: Biodegradation Model Parameters Definition

Equation 8.27a, 8.28b and 8.29c must be solved simultaneously by numerical methods. Because of time limits, the quantitive solution of the biodegradable model is not described in this chapter. But the qualitive description of the biodegradation model with experimental data will be discussed in the following.

# **8.5 MODEL DISCUSSION**

# 8.5.1 Surface Area

From equation 8.27a, 8.27b and 8.27c, it can be seen that the specific surface area is not included in any terms of the biodegradation model. It indicates that the specific surface area has no significant effect neither on mass transport flux nor biochemical rate. Enlargement of the specific surface area does not essentially change the physical, chemical and biological mechanisms. But it will enhance the total amount of mass flow and production of biochemical reaction, since:

$$M_{A} = J_{A} \bullet A$$

$$G_{A} = r_{A} \bullet A$$
(8.28)

Where  $M_A, G_A$  is the total mass flow and production, respectively, A is the area. Spendlin uses high surface area material – clay – as inert material for waste decomposition, the results did not show early methane production because the clay does not change the physical and biochemical reaction rate.

The incineration ash provides high surface area, thus enhances the gas production. However, the incineration ash also reaches early methane production, which indicates the incineration ash changes the biochemical reaction mechanism and rate.

# 8.5.2 Temperature

Temperature effects on this biodegradation model is shown by the temperature effects on the diffusion coefficient Dc, Dm, the rate constant Ks and the specific growth rate  $\mu_m$ .

The mass diffusivity is proportional to temperature.

The rate of biological activity doubles with every  $10^{\circ}$ C rise in temperature within the range 5-35 °C , and rapidly decrease in growth rate as the temperature increases above  $35^{\circ}$ C and falls to zero as the temperature approaches  $45^{\circ}$ C.

# 8.5.3 Moisture Content

Moisture content and flow parameters are input data of this biodegradation model. Simulation results are then presented to show the impact of moisture contents on key variables such as fatty acid concentration, methanogenic biomass, and depletion of the solid organic fraction.

Moisture effects on this biodegradation model is shown on both the hydrolysis rate and the mass transport rate.

From equation 8.26, it can be seen that the hydrolysis rate increases with moisture content. The moisture content has determined the flow rate u and thus effects the mass transport rate between the liquid phase and the solid phase.

Comparing the experimental data of the municipal solid waste with leachate recycling and without leachate recyling, recyling the leachate will significantly improve the moisture content and the flow rate, therefore promote the rate constant one order of magnitude higher.

Comparing the experimental data of the MSW and MSW+HSWi reactor, the incineration ash has higher water-hold ability resulting in a higher moisture content, and thus enhances the biodegradation process.

# 8.5.4 Initial Organic Concentration

The initial organic concentration  $S_0$  will effect the hydrolysis rate.

If the initial organic concentration higher, the hydrolysis rate becomes higher. But this does not mean early methane production because hydrolysis may result in accumulation of fatty acid and thus the higher fatty acids concentration will increase product inhibition.

Comparing the experimental data of MSW, MSW+HSWs and MSW+HSWi reactors, the high initial concentration of organic waste fraction does not lead to early methane production. On the contrary, the mixture of MSW and hospital waste preatment residues reach enhancement because of dilution effect.

# 8.5.5 Fatty Acids Concentration

The fatty acids concentration has effects on both the methanogenic biomass growth rate and hydrolysis rate. The higher fatty acids concentration may promote the reaction rate of methanogenic biomass growth, but it will decrease the hydrolysis rate because of product inhibition. So there is an optimal range for fatty acid concentration (pH between 6.5 to 8) at which the methanogenic biomass growth rate equals to the fatty acids accumulation rate. If there is a buffering material for pH and keep in this optimal range, the methane production can be significantly promoted.

The incineration ash can not only neutralize the pH to the optimal pH range, but also can buffer the pH value and keep within the optimal range. As the experimental data show, the methane production has been significantly improved.

# 8.5.6 THE EFFECTS OF INITIAL METHANOGENIC BIOMASS CONCENTRATION ON BIODEGRADATION MODEL

Initial methanogenic biomass concentration effects the fatty acids concentration. It will significantly effect the accumulation of fatty acids. When there is no initial methanogenic biomass, accumulation of fatty acids will result in product inhibition. Obviously, higher initial methanogenic biomass concentration will significantly overcome the product inhibition of fatty acids. This was proved in practice by addition of sludge or composting material.

# **Chapter 9 Conclusion and Outlook**

This research investigated first the biodegradability of sterilized hospital waste and the leaching behavior of hospital waste incineration ash in comparison with municipal solid waste, then co-disposal of sterilized hospital waste with municipal solid waste, and co-disposal of hospital waste incineration ash with municipal solid waste. The results provide the first concrete data for the fate of hospital waste after incineration and sterilization pretreatment under landfill conditions, and their effects on a municipal solid waste landfill site. All together these data provide a basis to set up an optimal hospital waste management. In addition, the research reveals that hospital waste incineration ash has several aspects advantageous for enhancement of organic decomposition and methane production, which might open a starting point with a novel approach to use incineration ash in general as an additive for organic fermentation.

Following conclusions can be drawn based on the research results:

- Biodegradability of Sterilized Hospital Waste
- 1 The biodegradable carbon content of the sterilized hospital waste is 0.04 kg Biod.C/ kg dry waste, which is 27% of that of municipal solid waste
- 2 The total theoretical gas amount of sterilized hospital waste is 0.08 m3/kg dry waste, which is 25% of that of municipal solid waste.
- 3 The accumulative gas amount of sterilized hospital waste by laboratory test is 10% of that of municipal solid waste. Landfill gas composition development of sterilized hospital waste is similar as the municipal solid waste. The sterilized hospital waste generates less amount of landfill gas than the municipal solid waste, but the quality of the landfill gas is the same as that of municipal solid waste.
- 4 Sterilized hospital waste undergoes the same biodegradation processes as municipal solid waste, but the gas production amount and rate seems lower than municipal solid waste due to lower amount of biodegradable material and worse conditions for bacteria inoculation than municipal solid waste.
- 5 The conversion from butyric acid to acetic acid might become the rate controlling step for the biodegradation process.
- 6 Sterilized hospital waste has less COD and organic load on leachate treatment than municipal solid waste due to lower organic content inside the waste materials than in the municipal solid waste. For the same reason, pH value is a little higher in the HSWs reactor than MSW reactor.

- Co-disposal of Sterilized Hospital Waste with Municipal Solid Waste
- 1 Co-disposal of sterilized hospital waste does not change the gas composition of the municipal solid waste. The quality of the landfill gas of mixture of sterilized hospital waste and municipal solid waste is the same as that of pure municipal solid waste.
- 2 Co-disposal of sterilized hospital waste with municipal solid waste does not change the pH, COD, and fatty acids concentrations of the leachate of municipal solid waste.
- 3 Co-disposal of sterilized hospital waste with municipal solid waste does not change the lag time and methane developing rate of municipal solid waste or pure sterilized hospital waste. This may indicate that lag time and the methane developing rate do not depend on the waste composition within a certain range, to a great extent it may depend on the external environmental conditions such as oxygen, pH and alkalinity, temperature, moisture. When these conditions keep the same, the biochemical reaction rate keeps the same.
- 4 The biodegradation of mixture of sterilized hospital waste and municipal solid waste is not only better than pure municipal solid waste, but also better than pure sterilized hospital waste. This can be explained by the better conditions for bacteria inoculation for sterilized hospital waste when it is mixed with municipal solid waste.
- 5 Sterilized hospital waste can be mixed together with municipal solid waste and be sent to household waste landfill site. It has no significant effects on the leachate quality of municipal solid waste landfill site, but it can enhance the biodegradation by providing wider surface area for organic mass transport.
- Leaching Behavior of Hospital Waste Incineration Ash
- 1 The hospital waste incineration ash contains higher content of calcium, manganese and magnesium than sterilized hospital waste and municipal solid waste, but shows no serious heavy metal leaching problem.
- 2 The hospital waste incineration ash has no biodegradability under landfill condition because it has no biodegradable organics content.
- 3 The pH value of the leachate from hospital waste incineration ash reactor is highly alkaline, due to the dissolution of alkaline reacting compounds, as for example the metal oxides and their salts, hydroxides and carbonates containing inside the incineration ash.

- Co-disposal of Hospital Waste Incineration Ash with Municipal Solid Waste
- 1 When un-biodegradable incineration ash was mixed with municipal solid waste, dramatically enhanced gas production of the municipal solid waste was proved.
- 2 Incineration ash provides a wide surface area and water-hold ability to accelerate the hydrolysis stage of biodegradation and thus accelerates the methane generation.
- 3 Incineration ash not only simply dilutes the organic acids, but also neutralizes the pH, shift the equilibrium and thus accelerates the acetogenic stage of waste biodegradation.
- 4 Incineration ash provides sufficient metal oxides and alkalinity for neutralization and buffer of pH-value, keep an optimal pH range for methanogenic bacteria growth and thus enhance the waste biodegradation.
- 5 The cations of the incineration ash may effect the rate of methane formation and may also provide sufficient nutrients for anaerobic ecosystem. It can be used as a resource material for anaerobic process.

Incineration ash combines a number of advantageous aspects for methane production process and thus can accelerate the biodegradation and enhance the stabilization of landfill sites.

Besides, the incineration ash can reduce the organic content and COD concentration of the leachate. It needs less energy on the leachate treatment for the organics, but the high salt content of the leachate may add big load to the leachate treatment.

# Gas Production Kinetic Model

Based on the derivation of enzyme reaction rate and micro-organism growth rate, a two-stage model combining zero-order and first-order kinetics is proposed.

This model combines the advantages of zero-order kinetic model and first-order kinetic model. It can simulate the actual landfill process more precisely and explain in a better way the mechanism of combining effect factors under landfill conditions.

At the first period, from waste placement until the peak value of gas production, the amount of substrate is not the limiting factor for biodegradation because we can propose substrate is sufficient for all type of bacteria. Therefore, other factors such as pH, moisture, nutrients, temperature, surface area etc. become the limiting factors for gas production rate. These factors may affect the lag time and the period to reach peak value of gas production in one hand, on the other hand may affect the total gas amount.

At the second period, when substrate is not sufficient for all bacteria, substrate concentration becomes the limiting factor. Under this condition, bacteria compete for substrate. Those bacteria who consume less energy will dominate the biodegradation

process. In this case, the bacteria responsible for hydrolysis, acetogenisis and methanogenis need to coordinate and form an optimal combination for this ecosystem. According to the experimental data, this model is good for simulation of the accumulative gas production and substrate concentration, but causes bigger error when it is used to simulate the instantaneous gas production rate because the assumption for this model is that the micro-organism concentration during all biodegradation process does not change. However, actually the micro-organisms concentration is not always constant. Especially initially there is a short period for bacteria growth after waste placement. In this period, the error of the model compared with actual landfill gas production rate may become bigger because the constant micro-organism concentration assumption is not the true situation. However, compared with the whole biodegradation process, the error from this short period has no big effect on the gas prediction for long-term landfill condition.

# • Diffusion Model for Organic Decomposition

Based on the molecular diffusion, mass transfer by moisture flow, enzyme-catalysed reaction rate and microbial growth rate, a diffusion model for organic biodegradation was derived.

This model combines mass transport terms and biochemical reaction rate. It concerns the affecting factors on hydrolysis, acidogenisis and methanogenisis processes, and the intricate relation between the different stages of waste biodegradation process.

The qualitive description of the biodegradation model fits with experimental data.

Because of financial restrictions, the following points have not yet been carried out and need further investigation:

- 1, Dioxin and elemental analysis of the incineration ash
- 2, Ion species and concentration of the leachate
- 3, Biodegradability of the leachate

# References

- [1] Hagenmaier. H., M. Kraft. H. Brunner and R. Haag (1987), Catalytic Effects of Fly Ash from Waste Incineration Facilities on the Formation and Decomposition of PCDDs and PCDFs, Env. Sci. Tech., 21, 1080-1084.
- [2] A.I. Zacharof, A.P. Butler. (1999) Modelling Biodegradation Processes in Heterogeneous Landfill Waste. Proc. 7th int. Landfill Symp., Thoms H. Christensen, Sardinia, 95-6102.
- [3] Lee Y-H. & Fan L.T. (1982) Kinetic Studies of Enzymatic Hydrolysis of Insoluble Cellulose: (1) Analysis of the Initial Rates. Biotechn. & Bioeng., 24, 2383-2406.
- [4] Lee Y-H., Fan L.T. (1983), Kinetic Studies of Enzymatic Hydrolysis of Insoluble Cellulose:
  (2) Analysis of Extended Hydrolysis Times. Biotechn. & Bioeng., 1983, 25, 939-966.
- [5] Larry D. Benefield and Clifford W. Randall (1980), Biological Process Design for Wastewater Treatment, Prentice-Hall, Englewood Cliffs.
- [6] Thomas H. Christensen and Peter Kjeldsen, (1989) Basic Biochemical Processes in Landfills, Sanitary Landfilling, Academic Press Limited, London, 29-49
- [7] Oremland R.S. and Polcin S. (1982), Methanogenesis and Sulphate Reducation: Competitive and Noncompetitive Substrates in Estuarine Sediments, Applied and Environmental Microbiology 44, 1270-1276
- [8] Stegmann R. and Spendlin H.-H. (1985), Research Activities on Enhancement of Biochemical Processes in Sanitary Landfills, Paper presented at the Conference 'New Directions and Research on Enhancement of Biochemical Processes in Sanitary Landfills', June 23-28, University of British Columbia, Vancouver, Canada.
- [9] Heuvel J.C. van der (1985), The Acidogenic Dissimilation of Glucose: a Kinetic Study of Substrate and Product Inhibition, Laboratory of Chemical Engineering, University of Amsterdam, The Netherlands.
- [10] McCarty P.L. and McKinney R.E. (1961), Volatile Acid Toxicity in Anaerobic Digestion, Water Pollution Control Federation Journal 33, 223-232.
- [11] Kugelman I.J. and Chin K.K. (1971), Toxicity, Synergism and Antagonism in Anaerobic Waste Treatment Processes, Anaerobic Biological Treatment Processes, Advances in Chemistry Series 105, 55-90.
- [12] Buivid M.G. (1980), Laboratory Simulation of Fuel Gas Production Enhancement from Municipal Solid Waste Landfills, Dynatech R & D Co., Cambridge, MA, USA
- [13] Rees J.F. (1980), The Fate of Carbon Compounds in the Landfill Disposal of Organic

Matter, Journal of Chemical Technology and Biotechnology 30, 161-175.

- [14] Rainer Stegmann (1996), Landfill Gas Utilization: an Overview, Landfilling of Waste: Biogas, E & FN Spon, London.
- [15] Christensen T.H., Cossu R., Stegmann R. (1992), Landfilling of Waste: Leachate, Elsevier Science Publishers LTD, England.
- [16] Tanja Scheelhaase, Asrid Halfmann (1998), Versuchsreaktoren zur Simulation von Deponieverhalten, Studienreihe Abfall-Now Band 18, Stuttgart, Bauhaus-Universitaet Weimar.
- [17] T.H. Christensen, R. Cossu, R. Stegmann, Landfilling of Waste: Biogas (1996), E&FN Spon, London.
- [18] George Tchobanoglous, Integrated Solid Waste Management(1993), McGraw-Hill, United States of America, P81
- [19] Rainer Stegmann, Hans-Henning Spendlin (1987), Enhancement of Biochemical Processes in Sanitary Landfills, In Proceedings of ISWA – International Sanitary Landfill Symposium 1987
- [20] Spendlin Hans-Henning (1991), Untersuchungen zur fruehzeitigen Initiierung der Methanbildung bei festen Abfallstoffen, Economica-Verl, Bonn.
- [21] Klaus Mudrack, Sabine Kunst (2003), Biologie der Abwasserreinigung, Spektrum Akademischer Verlag Heidelberg, Berlin.
- [22] Cecchi F., Traverso, P.G., Claney. (1988) State of the Art of R&D in Anaerobic Digestion Process of Municipal Solid Waste in Europe. Biomass, 16, 257-284.
- [23] Wang Z. & Banks C.J. (2000) Accelerated Hydrolysis and Acidification of Municipal Solid Waste in a Flushing Anaerobic Bio-reactor Using Treated Leachate Recirculation. Waste Man. & Res., 18, 215-230.
- [24] Barlaz M.A., Ham R.K. & Schaefer D.M (1989), Mass Balance Analysis of Anaerobically Decomposed Refuse. A.S.C.E., J. Env. Eng. Div, 115,6, 1088-1102.
- [25] Bookter T.J. & Ham R.K (1982), Stabilization of Solid Waste in Landfills. A.S.C.E., J. Env. Eng. Div, 108, EE6, 1089-1100.
- [26] Wald S., Wilke C.R. & Blanch H.W (1984), Kinetics of the Enzymatic Hydrolysis of Cellulose. Biotechn. & Bioeng. 26, 221-230
- [27] Mcdougall J.R., Pyrah I.C (1999), Moisture Effects in a Biodegradation Model for Waste Refuse. Proc. 7th int. Landfill Symp., T. H. Christensen, Sardinia, 59-66
- [28] Zacharof A.I. and Butler A.P. (1999), Modelling Biodegradation Processes in Heterogeneous Landfill Waste, Landfill Processes and Waste Pre-treatment,
Proceedings of Seventh International Waste Management and Landfill Symposium, Sardinia.

### Appendix

1 Gas Production Rate Kinetic Model for Co-disposal of Sterilized H	lospital Waste
with Municipal Solid Waste	105
2 Gas Production Rate Kinetic Model for Co-disposal of Hospital Wast	te Incineration
Ash with Municipal Solid Waste	109
3 Gas Production Rate Kinetic Model for Municipal Solid Waste with	nout Leachate
Recycling	114
4 Gas Production Rate Kinetic Model for Sterilized Hospital Waste with	hout Leachate
Recycling	118

#### 1 GAS PRODUCTION RATE KINETIC MODEL FOR CO-DISPOSAL OF STERILIZED HOSPITAL WASTE WITH MUNICIPAL SOLID WASTE

Use the kinetic model to the landfill reactor for mixture of sterilized hospital waste and municipal solid waste which was described in Chapter 5.

C<sub>01</sub>=114 g Biod.C/kg dry waste

Fig. 1 shows the experimental accumulative gas production development with time.

Fig. 2 shows the experimental substrate concentration development with time.

Fig. 3 shows the experimental gas production rate development with time.

From the figures it can be clearly seen that the time of the end of peak value of gas production:



p=80 days

Fig. 1: Gas Production of MSW+HSWs Reactor



Fig. 2: Substrate Concentration of MSW+HSWs Reactor



Fig. 3: Gas Production Rate of MSW+HSWs Reactor

From 0-80 days, use linear simulation to the curve of substrate concentration, the rate constant  $k_1$  can be achieved:

From 80-150 days, use logarithmic simulation to the curve of substrate concentration, the rate constant  $k_2$  can be achieved:

$$k_2 = 0.0038 \text{ day}^{-1}$$

So,

$$C_{02} = C_{01} - k_1 p = 76.5 g Biod.C/kg dry waste$$

Then the kinetic model for MSW+HSWs reactor with leachate recycling is expressed in

following:

$$C_{t} = 114 - 0.4687t, t = [0,80]$$
  

$$C_{t} = 76.5e^{-0.0038(t-80)}, t = [80, t]$$
(1)

The accumulative gas production kinetic model can be got out from equation 7.32 and is shown in the following:

$$G = 0.8751t, t = [0,80]$$
  

$$G = 213 - 143e^{-0.0038(t-80)}, t = [80, t]$$
(2)

Gas production rate can be derived from equation 7.33:

$$\frac{dG}{dt} = 0.8751, t = [0,80]$$

$$\frac{dG}{dt} = 0.5427e^{-0.0038(t-80)}, t = (80,t]$$
(3)

Fig. 4 illustrates the comparison with model data and experimental data.

It can be seen that model data fits to experimental data very well on substrate concentration and accumulative gas product. But for the instantaneous gas production rate of the initial period, model data do not fit the experimental data. The reason might be the fluctuant bacteria concentration in the laboratory landfill reactor.

The biggest relative error for substrate concentration between model data and experimental data is 12.7%.

The biggest relative error for accumulative gas production between model data and experimental data is 13.0%.

The biggest error for instantaneous gas production rate between model data and experimental data is 51.9%







Fig. 4: Model Data Versus Experimental Data for MSW+HSWs Reactor

#### 2 GAS PRODUCTION RATE KINETIC MODEL FOR CO-DISPOSAL OF HOSPITAL WASTE INCINERATION ASH WITH MUNICIPAL SOLID WASTE

Use the kinetic model to the landfill reactor of the mixture of incineration ash and municipal solid waste with leachate recycling which was described in Chapter 6. The initial substrate concentration of municipal solid waste:

C<sub>01</sub> = 174 g Biod.C/kg dry waste

Fig. 5 shows the experimental accumulative gas production development with time.

Fig. 6 shows the experimental substrate concentration development with time.

Fig. 7 shows the experimental gas production rate development with time.

From the figures it can be clearly seen that the time of the end of peak value of gas production:



p = 80 day

Fig. 5: Gas Production of MSW+HSWs Reactor



Fig. 6: Substrate Concentration of MSW+HSWs Reactor



Fig. 7: Gas Production Rate of MSW+HSWs

From 0-80 days, use linear simulation to the curve of substrate concentration, the rate constant  $k_1$  can be achieved:

 $k_1 = 2.7991$  g Biod.C/ (kg dry waste\*day)

Then substrate concentration can be calculated as:

$$C_t = 174 - 2.7991t, t = [0,80]$$
 (4)

In order to use logarithmic simulation to the second period, here definite:

$$C'_t = C_t + 100$$
 (5)

From 80-150 days, use logarithmic simulation to the curve of substrate concentration, the rate constant  $k_2$  can be achieved:

Then the kinetic model for MSW reactor with leachate recycling is expressed in following:

$$C_{t} = 174 - 2.7991t, t = [0,80]$$
  

$$C_{t} = 50e^{-0.0355(t-80)} - 100, t = [80, t]$$
(6)

The accumulative gas production kinetic model can be got out from equation 7.32 and is shown in the following:

$$G = 5.2259t, t = [0,80]$$
  

$$G = 511.6 - 93.4e^{-0.0355(t-80)}, t = [80,t]$$
(7)

Gas production rate can be derived from equation 7.33:

$$\frac{dG}{dt} = 5.2259, t = [0,80]$$

$$\frac{dG}{dt} = 3.3139e^{-0.0355(t-80)}, t = (80,t]$$
(8)

Fig. 8 illustrates the comparison with model data and experimental data.

It can be seen that model data fits to experimental data very well on substrate concentration and accumulative gas product. But for the instantaneous gas production rate of the initial period, model data do not fit the experimental data. The reason might be the fluctuant bacteria concentration in the laboratory landfill reactor.

The biggest relative error for substrate concentration between model data and experimental data is 14.5%.

The biggest relative error for accumulative gas production between model data and experimental data is 12.8%.

The biggest error for instantaneous gas production rate between model data and experimental data is 113%







Fig. 8: Model Data Versus Experimental Data for MSW+HSWs Reactor

#### 3 GAS PRODUCTION RATE KINETIC MODEL FOR MUNICIPAL SOLID WASTE WITHOUT LEACHAT RECYCLING

Use the kinetic model to the landfill reactor of the municipal solid waste without leachate recycling which was described in Chapter 4.

The initial substrate concentration of municipal solid waste:

C<sub>01</sub> = 105 g Biod.C/kg dry waste

Fig. 9 shows the experimental accumulative gas production development with time.

Fig. 10 shows the experimental substrate concentration development with time.

Fig. 11 shows the experimental gas production rate development with time.

From the figures it can not be clearly seen that the time of the end of peak value of gas production. Because this reactor was running without leachate recycling, the substrate degradation is much slower than that with leachate recycling. Hence, the substrate concentration is always sufficient for all bacteria during all the simulation process and does not reach the second period. We can propose that substrate concentration is not the limiting factor and this reactor follows a zero-order kinetic for all the simulation time.



Fig. 9: The Experimental Accumulative Gas Production development with Time for MSW without Leachate Recycling



Fig. 10: The Experimental Substrate Concentration Development with Time for MSW without Leachate Recycling



Fig. 11: The Experimental Gas Production Rate Development with Time for MSW without Leachate Recycling

Use linear simulation for the substrate concentrate curve, we can get:

 $k_1 = 0.0255 \text{ g Biod.C/} (\text{kg dry waste*day})$ 

Then the kinetic model for MSW reactor without leachate recycling is expressed in following:

$$C_t = 105 - 0.0255t \tag{9}$$

The accumulative gas production kinetic model can be got out from equation 7.32 and is shown in the following:

$$G = 0.0476t$$
 (10)

Gas production rate can be derived from equation 7.33:

$$\frac{dG}{dt} = 0.0476 \tag{11}$$

Fig. 12 illustrates the comparison with model data and experimental data.

The biggest relative error for substrate concentration between model data and experimental data is 0.7%.

The biggest relative error for accumulative gas production between model data and experimental data is 37.0%.

The biggest error for instantaneous gas production rate between model data and experimental data is 64.1%





Fig. 12: Model Data versus Experimental Data for MSW Reactor without Leachate Recycling

#### 4 GAS PRODUCTION RATE KINETIC MODEL FOR STERILIZED HOSPITAL WASTE WITHOUT LEACHAT RECYCLING

Use the kinetic model to the landfill reactor of the sterilized hospital waste without leachate recycling which was described in Chapter 4.

The initial substrate concentration of municipal solid waste:

C<sub>01</sub> = 42 g Biod.C/kg dry waste

Fig.13 shows the experimental accumulative gas production development with time.

Fig. 14 shows the experimental substrate concentration development with time.

Fig. 15 shows the experimental gas production rate development with time.

From the figures it can be seen that after70 days, no significative gas produces in this reactor. The biodegradable organics is still available but the bacteria is not active because obviously the bacteria inoculation is not very successful. We can propose during all the simulation process substrate concentration does not reach the second period. We can propose that substrate concentration is not the limiting factor and this reactor follows a zero-order kinetic from initial period to 70 days of simulation time.



Fig.13: The Experimental Accumulative Gas Production Development with Time for HSWs



Fig. 14: The Experimental Substrate Concentration Development with Time for HSWs



Fig. 15: The Experimental Gas Production Rate Development with Time for HSWs.

Use linear simulation for the substrate concentrate curve, we can get:

 $k_1 = 0.0098$  g Biod.C/ (kg dry waste\*day)

Then the kinetic model for MSW reactor without leachate recycling is expressed in following:

$$C_t = 42 - 0.0098t \tag{12}$$

The accumulative gas production kinetic model can be got out from equation 7.32 and is shown in the following:

$$G = 0.0183t$$
 (13)

Gas production rate can be derived from equation 7.33:

$$\frac{dG}{dt} = 0.0183 \tag{14}$$

Fig. 16 illustrates the comparison with model data and experimental data.

The biggest relative error for substrate concentration between model data and experimental data is 0.4%.

The biggest relative error for accumulative gas production between model data and experimental data is 27.3%.

The biggest error for instantaneous gas production rate between model data and experimental data is 42.1%





Fig. 16: Experimental Data Versus Model Data for HSWs

# Resume

### **Qin Wang**

- Birthday: 1971, 08, 06
- Birthplace: Emei P.R.China

## Education:

1992, 09 1996, 07	Sichuan University, Chemical
	Processing Machinery, Bachelor (china)
1996, 09 1999, 07	Sichuan University, Chemical
	Processing Machinery, Master (china)
2001, 09 2002, 09	Zhejiang University, Environmental
	Engineering, Ph.D. Student (china)
2002, 10 2004, 12	Duisburg-Essen University, Environmental
	Engineering, Ph.D. Student (Germany)

## Work Experience:

1999, 07 2000, 07	University of Shanghai for Science and
	Technology, Lecturer (china)
2000, 09 2001, 08	TOP Institute for Information and Technology,
	Lecturer (china)