THESIS APPROVAL

GRADUATE SCHOOL, KASETSART UNIVERSITY

Master of Engineering (Environmental Engineering)

DEGREE

Environmental Engineering	Environmental Engineering
FIELD	**DEPARTMENT**

TITLE: The Effect of Volatile Fatty Acid on Migration of Heavy Metals from Stabilized Hazardous Waste in Secured Landfill

NAME: Mr. Koedkao Peeratiyuth

THIS THESIS HAS BEEN ACCEPTED BY

______________________________ **THESIS ADVISOR**

(Mr. Suchart Leungprasert, Ph.D.)

______________________________ **THESIS CO-ADVISOR**

(Assistant Professor Cheema Soralump, Ph.D.)

______________________________ **DEPARTMENT HEAD**

(Assistant Professor Mongkol Damrongsri, Dr. Ing.)

APPROVED BY THE GRADUATE SCHOOL ON ______________________________

______________________________ **DEAN**

(Associate Professor Gunjana Theeragool, D.Agr.)

THESIS

THE EFFECT OF VOLATILE FATTY ACID ON MIGRATION OF HEAVY METALS FROM STABILIZED HAZARDOUS WASTE IN SECURED LANDFILL

KOEDKAO PEERATIYUTH

A Thesis Submitted in Partial Fulfillment of
the Requirements for the Degree of
Master of Engineering (Environmental Engineering)
Graduate School, Kasetsart University

2010

ACKNOWLEDGEMENTS

I would like to express my gratitude to all those who gave me assistance and ultimately enable me to complete this thesis. Thank you all Kasetsart university laboratory staffs Mrs. Piyakorn Boonsuwan, Mrs. Kanchana Thuyviang and Mr. Prachaya Junsak whose gave me a lot of technical advice, helping hand and comfortable working environment. Special thanks to Mrs. Suppajee Pornpongmetta for guiding my way through laboratory session.

I would also like to thank GENCO Company Ltd and Kasetsart's energy research institution for assistance in transportation of the stabilized hazardous waste samples from Ratchaburi province for research.

I would like to grateful thank and deeply indebted Dr. Suchart Leungprasert my thesis advisor for valuable advice and support for writing of this thesis. Lastly, thank you my family for constant love, support, patient and understanding.

Koedkao Peeratiyuth
April 2010

TABLE OF CONTENTS

	Page
TABLE OF CONTENT	i
LIST OF TABLES	ii
LIST OF FIGURES	v
LIST OF ABBREVIATION	vii
INTRODUCTION	1
OBJECTIVES	3
LITERATURE REVIEW	5
MATERIAL AND METHOD	24
Materials	24
Methods	25
RESULT AND DISCUSSION	33
Result	33
Discussion	51
CONCLUSION AND RECOMMENDATION	57
Conclusion	57
Recommendation	59
LITERATURE CITED	60
APPENDICES	64
Appendix A Stabilized Hazardous Sludge Analysis	65
Appendix B Leachate Analysis	79
Appendix C Gas analysis	97
Appendix D International Conference	104
CURRICULUM VITAE	109

LIST OF TABLES

Table **Page**

1 Anaerobic reactor dimension **Source:** Qin Wang, (2004) 11

2 Rachaburi's average 30 years monthly rainfall data 26

3 Phase 1 & 2 Waste Characteristics prior to reactor operation 33

4 Amount of 0.25N Acetic acid added 34

5 Phase 2: Waste Characteristics after reactor operation 41

6 Phase 3: Waste Characteristics prior to experiment 42

7 Phase 3: Gas chromatography result 44

8 Phase 3: Waste Characteristics after reactor operation 47

Appendix Table

A1 Initial Sludge Analysis TS, FS, VS and Moisture parameter prior to phase 1 and phase 2 operation 66

A2 Phase 2: Raw Data of Sludge Analysis TS, FS, VS and Moisture parameter after phase 2 67

A3 Phase 2: Summary of Sludge Analysis TS, FS, VS and Moisture parameter after phase 2 68

A4 Phase 2: Initial TOC analysis 69

A5 Phase 2: Raw data of TOC analysis after 90 days reactors operation 70

A6 Phase 2: Summary of TOC analysis after 90 days reactors operation 71

LIST OF TABLES (Continued)

Appendix Table		Page
A7	Phase 3: Summary of sludge analysis TS, FS, VS and Moisture parameter prior to phase 3	72
A8	Phase 3: Raw data of sludge analysis TS, FS, VS and Moisture	73
A9	Phase 3: Summary of sludge analysis TS, FS, VS and Moisture parameter after phase 3	74
A10	Phase 3: Raw data of initial TOC analysis	75
A11	Phase 3: Summary of phase 3 initial TOC analysis	76
A12	Phase 3: Raw data of TOC analysis after 75 days reactors operation	77
A13	Phase 3: Summary of TOC analysis after 75 days reactors operation	78
B1	Phase 1: Heavy metal analysis of extract fluid	80
B2	Phase 1 raw data: Heavy metal analysis of extract fluid by AAS	81
B3	Phase 2 raw data: VFA analysis of leachate	83
B4	Phase 2 raw data: pH analysis of leachate	85
B5	Phase 2 raw data: Cd analysis of leachate by AAS	87
B6	Phase 2 raw data: Cr analysis of leachate by AAS	88
B7	Phase 3 raw data: pH analysis of leachate	89
B8	Phase 3 raw data: VFA analysis of leachate	91
B9	Phase 3: COD analysis of leachate	93
B10	Phase 3 raw data: TDS analysis of leachate	95
C1	Phase 2 raw data: Gas production measurement	98

LIST OF TABLES (Continued)

Appendix Table **Page**

C2 Phase 3 raw data: Gas production measurement 100

C3 Phase 3: GC6890 Agilent Gas chromatography raw data 102

LIST OF FIGURES

Figures		Page
1	Substrate utilize by microorganism within landfill	9
2	USEPA Method 1684 TS,VS, FS and Moisture content	13
3	TOC analytical procedures using TOC-Vsh / SSM	15
4	Distillation method for VFA analytical procedures	17
5	Schematic diagram of a gas chromatograph	18
6	Column partition chromatographic method: VFA determination	19
7	Titration method: VFA determination	20
8	Method 5220C Close reflux method for COD	21
9	Schematic diagram of Atomic absorption spectrophotometer	22
10	Solid (3051A) and liquid (3030E) sample preparation	23
11	Configuration of single pass landfill reactor	28
12	Phase 1 methodology	29
13	Phase 2 methodology	31
14	Phase 3 methodology	32
15	Leaching test result Heavy Metal vs pH	35
16	VFA concentration in leachate during phase 2 experiment	37
17	pH of leachate during phase 2 experiment	37
18	Cumulative gas production from 90 days operation	39
19	Cr and Cd leaching during reactor operation	40
20	Mass Balance of the system concerning TOC transformation	41

LIST OF FIGURES (Continued)

Figures		Page
21	Phase 3 pH of leachate sample	43
22	Phase 3: Cumulative gas production	44
23	Phase 3 Cumulative COD leached from reactors	45
24	Phase 3 Cumulative TDS leached from reactors	46
25	Phase 3 Cumulative VFA leached from reactors	47
26	VFA concentration in phase 3 experiment	49
28	COD concentration in phase 3 experiment	50
29	TDS concentration in phase 3 experiment	50
30	VFA/COD ratio for phase 3 simulated landfill reactors	53
31	Mass Balance of 3 simulated landfill reactors	55

LIST OF ABBREVIATION

AAS = Atomic Absorption Spectophotometer

BOD = Biological Oxygen Demand

$CaCO_3$ = Calcium Carbonate

COD = Chemical Oxygen Demand

FAS = Ferrous Ammonium Sulfate

FID = Flame Ionization Detector

FS = Fixed Solid

GENCO = General Environmental Conservation Public Co. Ltd.

HMs = Heavy Metals

MINTEQ = Minteq International Inc.

MSW = Municipal Solid Waste

NaOH = Sodium Hydroxide

PMMA = polymethylmethacrylate

PVC = Polyvinyl Chloride

SSM = Solid Sampling Module

TCD = Thermal Conductivity Detector

TCLP = Toxicity Characteristic Leaching Procedure

TC = Total Carbon

TDS = Total Dissolved Solid

TOC = Total Organic Carbon

TS = Total Solid

LIST OF ABBREVIATION (Continued)

USEPA = United State Environmental Protection Agency

VFA = Volatile Fatty Acid

VS = Volatile Solid

THE EFFECT OF VOLATILE FATTY ACID ON MIGRATION OF HEAVY METALS FROM STABILIZED HAZARDOUS WASTE IN SECURED LANDFILL

INTRODUCTION

In present time, increasing number of industrial facilities, household electrical appliances and synthetic chemical uses have contributed to increasing the amount hazardous waste generated. Hazardous waste has potentially caused a harmful effects to human health or the environment due to its chemical activity, toxicity, explosivity, ignitability and corrosivity characteristics whether alone or when coming to contact with other wastes (United Nation Environmental Programme [UNEP],1985). Hazardous waste usually persists on the environment for last period and causes adverse effect to any organism. Improper hazardous waste management and disposal causes significant land and groundwater contamination.

Due to danger impose by improper handling of hazardous waste material, proper hazardous waste management and disposal operations must be strictly regulated and controlled to ensure minimal risk of health and environmental aspects. Hazardous waste handling and disposal control system usually consist of legislation and regulation, enforcement procedure, provision of adequate facilities for hazardous waste treatment and disposal and public awareness. In general case, lime-stabilized pretreatment prior to bury at hazardous waste landfill site should be sufficiently retained heavy metals from leaching out. However heavy metals leached out more when a portion of organic content in the waste increased. This result occurred from an increase in microbial activity leading to the production of volatile fatty acids that could possibly dissolve the heavy metals from the stabilized hazardous waste. This finding led to this research topic on the end product occurring from microbial activity affecting heavy metals leaching. In this research, the end product was volatile fatty acids generated from secured landfill reactor.

This research focused on finding the relevant factors involved in pH reduction from the leachate which contributes to heavy metals migration from lime-stabilized hazardous waste. Changing of pH occurred due to biological reaction of biodegradable portion of hazardous waste, the anaerobic decomposition of biodegradable material can generate acidic condition which can disturb heavy-metal containing waste causing them to migrate and contaminate leachate. Although hazardous waste was stabilized and solidified with cement-lime process, it has still found some heavy metals and organic contents with very high concentrations in leachate from the secured landfill site in Thailand. Due to Thailand's regulation, hazardous waste is required to stabilize before disposal in the landfill. This situation is not usual because normally at pH of 12 any microbial activity should be inhibited resulting no organic concentration or its end products found in the leachate. The degradation of organic matter contained in the stabilized waste still occurred although the hazardous waste was stabilized at pH greater than 10. The objective of this research is to establish evidences showing that microbial activity is still continued under this extreme pH level. Further area of study will include investigation of minimum portion of hazardous biodegradable waste and hazardous heavy metal waste so that anaerobic decomposition (to be specific Acetogenesis process) will not disturb the waste containing heavy metals and further contaminate leachate.

OBJECTIVES

1. To determine the effect of volatile fatty acids added to stabilized hazardous waste on the leaching of heavy metals.

2. To investigate the microbial activity in anaerobic landfill reactors contained stabilized hazardous waste.

Scope of Study

The scope of this study including:

1. Parameters relating to microbial degradation including; Total organic carbon, Volatile fatty acids, Chemical oxygen demand, Total dissolved solid, Heavy metals, pH, Total solid, Volatile solid were measured.

2. The effect of volatile fatty acids added to stabilized hazardous waste on the leaching of heavy metals was investigated. During Phase 1 of experiment, acetic acid was used to represent volatile fatty acid generated by acidogen bacteria during laboratory scale leaching test. Acetic acid was used to adjust lime stabilized sludge and leachate pH varied from 10 to 6. Samples were prepared in 1:10 solid/liquid ratio and shaken for 18 hours according to TCLP procedures.

3. Phase 2 and Phase 3 experiments were conducted with 3 bench scale reactors. All reactors were operated under same conditions as replications. Rainwater addition quantity were estimated by using actual meteorological data of the region. The reactors were operated for 90 days for Phase 2 experiment and 75 days for Phase 3 experiment. Stabilized hazardous waste used was collected from a secured landfill site in Ratchaburi province.

4. Calculation of mass balance show portion of organic content within hazardous waste body converted to end product which result in migration of heavy metal into leachate. Then calculation can be used to estimate the actual amount of Total organic carbon consumed, heavy metal leached, volatile fatty acid production and gas production in Phase 3 secured landfill operation.

LITERATURE REVIEW

1. Landfill Waste Degradation Process

It is a process involving biochemical reaction by various culture of microbial organisms. The biochemical reaction cause by different species/culture of microbial activities within landfill are varies depending on which phase of degradation that waste undergoes. The factor affecting degradation are varies depending on phase of degradation, type of food source available, pH of waste body as well as the availability of different nutrient source.

From the statement of problem, source of organic acid introduced to system within secured landfill waste body must be monitor. From various recent study, biological reactions occurred inside landfill that can be divided into 5 phases. The critical phases in this thesis are phase 1,2 and 3 which are responsible for organic acid production. Anaerobic digestion can be divided into 3 sub stages (Taylor and Allen, 2006). which are;

1. Acidogenic (Acid) fermentation
2. Intermediate acetogenesis
3. Methanogenesis

1.1 Phase 1: Aerobic degradation (Hydrolysis #1)

First phase of biological degradation process is aerobic phase which mainly involve hydrolysis of solid waste. The part of wastes that are easily and readily degradable react with oxygen to form end product of carbon dioxide and water. The energy from exothermic reaction produced by metabolism of microorganism raise temperature within landfill to be higher thus promoting biological activity to next step. The aerobic decomposition is continue until trapped oxygen is used up. Hydrolysis reaction greatly affect microbial activity of degradation process. It is preliminary break down of long chain organic carbon molecule for further decomposition by both aerobic and anaerobic microbe. Lack of water in the system limit ability of microorganism to utilize carbon source. In early stage of landfill, acidogenesis and acetogenesis are robust and rapid processes which cause acetic acid to accumulate, at least until methanogenesis is established, whereupon hydrolysis becomes the rate-limiting step of whole operation. (Vavilin *et al.*, 2003), (Maharaj and Elefsiniotis, 2000)

1.2 Phase 2: Acidogenesis (Hydrolysis #2)

Phase 2 begin when oxygen are depleted and aerobic condition are replaced by anoxic/anaerobic conditions. Drop in oxygen indicate transition from initial aerobic to facultative anaerobic microbial. There will be lag time until favorable stabilization condition developed. In anaerobic phase, primary electron acceptor shifts from oxygen to nitrate and sulfate while carbon dioxide level increased. (Taylor and Allen, 2006). The indicator of completed transition is pH drops appear in leachate due to formation of organic acid. Substrate are converted to a usable form via enzyme which hydrolyzes organic polymers and lipid to fatty acids, protein to amino acids, polysaccharides to monosaccharide and nucleic acid to purines and pyrimidines. (Xian Qu *et al.*, 2008).

1.3 Phase 3: Acetogenesis

Acetogenic bacteria perform further hydrolysis and fermentation of intermediate product from previous acidogenic phase to usable product for methanogenic bacteria. The reason for this is that some intermediate product, without further breakdown to simple molecule is unusable by methanogenic bacteria. In Acetogenic fermentation phase, ferment hydrolysis products (amino acids, fatty acids and glycerol) are further breakdown to simple organic acids. Formation of organic acid and and its variation cause by affecting nature and type of intermediate product formed. Acidic leachate produced in this phase confirm to mobilized heavy metal species (Xian Qu *et al.*, 2008). Nutrients such as nitrogen and phosphorous are released and utilized by microorganism and possible removal of nutrient with leachate stream. Carbon dioxide bloom to the maximum potential as indicator of phase changes (Obuli P *et al.,* 2007). Acitogens ferment hydrolysis products to organic acid, acetic acid is more than 70%. The amount of Acetic acid produced by this phase should indicate biological activity inside stabilized hazardous waste which is a primary objective of the experiment.

The decrease in pH cause by production of volatile fatty acid is the main investigation issue on its effect toward lime-stabilize hazardous sludge and produce heavy metal contaminated leachate. However, volatile fatty acid generally not significant consumer of alkalinity in the system, therefore pH might not change unless significant amount of organic acid in the system.

1.4 Phase 4: Methanogenesis

Intermediate products from acidogenesis and acetogenesis process are utilize as methanogenic substrate (H2, CO2, formate, methanol, methylamine and acetate). These then further converted to methane and carbon dioxide as end product. During this phase pH level is elevate due to utilization of acetic acid (70% of methane are formed from degradation of acetic acid). Therefore the critical acidic leachete is not present in this phase of degradation. Characteristic of this phase can be observe by dropping of BOD, COD and conductivity of leachate (Taylor and Allen, 2006).

In intermediate anaerobiosis phase and methanogenic fermentation phase, volatile fatty acid is used with Carbon dioxide and hydrogen for generation of methane by methanogen. Methane and acid production proceed simultaneously, acid production rate is slowly reduced due to depletion of carbon source therefore pH will eventually return to neutral range. However if amount organic acid produced exceed methanogen's demand, it may cause methane generation microorganism to die. Methanogenesis only survive in narrow pH range of 6.5 - 8 (Martin, A.D. 2007).

2. Anaerobic microbiology

Theoretically, least 3 groups of bacteria are involve in anaerobic degradation process

1. Hydrolysis and acid-forming (Acidogenic) bacteria
2. Acetic acid and hydrogen-forming (Acetogenic) bacteria
3. Methane-forming (Methanogenic) bacteria
4. Denitrifying bacteria

Anoxic biogeochemical cycle of carbon is the main focus of microbe activity within landfill. Mixed cultures of microorganism are containing within landfill all attributed to different trophic groups. Cooperation between two metabolically different types of bacteria that are depending on each other is call syntrophic association (American Society for Microbiology, 1975). Acetogen is bacteria that generate acetate as product of anaerobic respiration. Acetogenic metabolism involves uses of carbon dioxide as carbon source and hydrogen as energy source. Polymer degrading microbes (acidogen) are degrading complex organic polymers into simple monomers which then further process by fermenting microbe or homoacetogens. The final intermediate product of acetate, hydrogen and carbon dioxide from acetogenesis then are further utilize by methanogens. 70% of methane is produced by degradation of acetic acid (aceticlastic methanogenesis) and about 30% by a redox reaction of hydrogen and carbon dioxide (hydrogenotrophic methanogenesis) (Roediger *et al.*, 1990).

First during hydrolysis most water-insoluble bipolymers such as carbohydrate, protein and fat are decomposed by extra-cellular enzymes to water-soluble monomers (amino acid, glucose, fatty acid) thus make them suitable for further degradation. In second acidification step, intermediate from hydrolysis are converted into acetic acid, hydrogen and carbon dioxide to be further process by methanogenic bacteria. However while some of intermediate product can be directly degrade bu acidogenic bacteria to end product to be utilize by methanogenic bacteria. Some of long chain fatty acid and alcohol molecule must be decomposed by acetogenic bacteria in order to be utilized by methanogenic bacteria.

During methane formation, acetic acid and hydrogen are substrate used by methanogenic bacteria to form methane gas and carbon dioxide. However group of methanogenic bacteria is formed of extreme obligate anaerobic micro-organism which are extremely sensitive to environmental changes. The mechanism behind this is very complex symbiotic relationship between methanogenic, sulfidogenic and acetogenic bacteria which working together to form a very low hydrogen partial pressure environment in which anaerobic fermentation can take place.

Rate-limiting step of whole anaerobic fermentation depend on characteristic of waste within landfill. If easily degradable substances dominate, methanogenesis of acetic acid is the rate-limiting factor (methane formation). If substances are harder to degrade, hydrolysis is the rate-limiting factor. However to achieve optimized undisturbed anaerobic degradation, speed of decomposition in consecutive steps should be equal

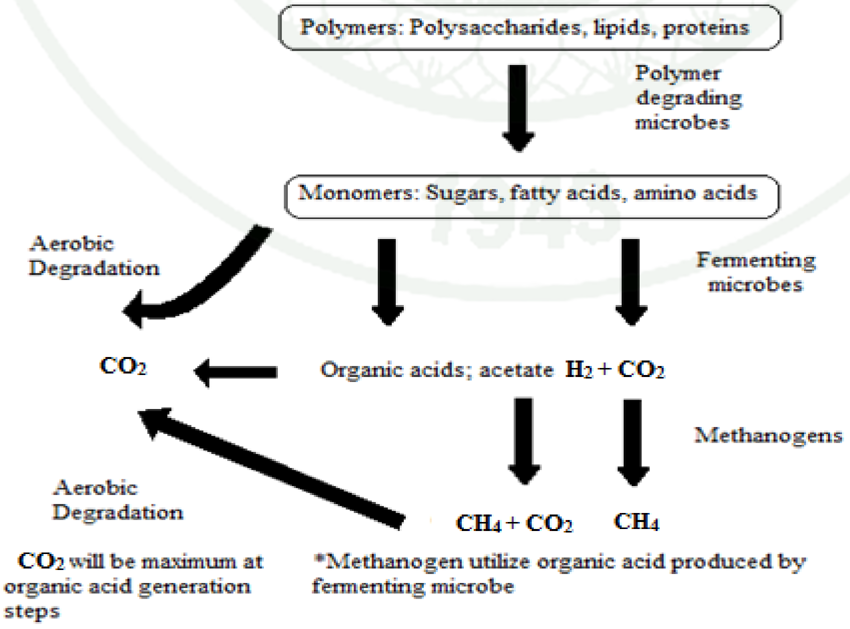


Figure 1 Substrate utilized by microorganism within landfill
Source: Rasche (1991)

3. Denitrification

Denitrifying bacteria are facultative heterotrophic organism, denitrification occurred only under anaerobic or anoxic condition. Denitrifying bacteria use nitrate as primary oxygen source and carbon source in waste body as its food. Nitrate are reduced to nitrogen gas. Important aspect of denitrification is the requirement for sufficient organic matter to drive the denitrification reaction. Therefore reduction of carbon source within system didn't depend entirely on either acidogenesis and methanogenic reaction but also denitrification as well.

Efficiency of denitrification depend on nitrate concentration, anoxic conditions, presence of organic matter, pH, temperature, alkalinity and the effects of trace metals. Denitrification can occur between 5 and 30°C (41°F to 86°F), pH of 7.0-8.5 and these rates increase with temperature and type of organic source present. Acetic acid and methanol are the carbon source that yield highest growth rate (The Water Planet Company, 2010). Lastly denitrification is an alkalinity producing process, approximately 3.0 to 3.6 pounds of alkalinity (as $CaCO_3$) is produced per pound of nitrate.

4. Reactor specification research

Information on designing simulated landfill reactor were obtained by looking at various research work such as laboratory simulation of in situ leachate treatment in semi-aerobic bioreactor landfill (Shou-liang Huo *et al.*, 2008) which involve construction of completely seal reactor simulating anaerobic condition. Reactors were made of polymethylmethacrylate (PMMA) of 1.5 cm thickness, with diameter of 20 cm and height of 1.2 m with effective volume of 31.4 liter. Reactors have 3 sample collection ports of solid waste set in the middle of reactors with 1 leachate outlet at the bottom. Leachate outlet was connected to leachate circulation tanks. 10 cm depth of pea gravel was placed at the bottom of the reactor to retain refuse and small particle. Reactor was sealed with silicone caulk and monitored for leak. Control reactor was operate with completely anaerobic condition while another reactor operated with installed air inlet. Reactor using peristaltic pump as water addition asparatus. In this work, water was sprayed at rate of 300ml per 6 days to increase moisture content of the waste. Another experiment investigating different hospital waste type biodegradation in Landfill constructed 3 anaerobic reactors with following dimension

Table 1 Anaerobic reactor dimension

	Pure sterilized hospital waste	Pure municipal solid waste	Pure hospital waste incineration ash
D(m)	0.28	0.21	0.29
H(m)	1	1	1

Source: Qin Wang, (2004)

With this information, reactor size and sampling point were determined and will be explain in further section. However another interesting finding is that if reactor was purge by nitrogen gas after sealed, anaerobic condition will be immediately established (Irem San *et al.*, 2001). We selected waste filling up to 73 cm similar to this reactor operation. This paper also suggests that leachate recirculation can enhance rate of landfill stabilization. However in this research, leachate are not recirculate just simple water addition to represent region's precipitation.

5. Researches of heavy metal leaching from landfill operation

Nonthawat's study involved investigation of total organic carbon contamination in secured landfill leachate. His finding reveal correlation of increased organic carbon contamination in stabilized hazardous waste and increased heavy metal leaching. (Nonthawat, 2008)

Xian Qu investigated heavy metal mobility in full-scale bioreactor landfill.

Scope of study on this research focus on initial stage of waste degradation. Result show that heavy metal rapidly leached out during initial 5 months then after methanogenic stage has been established, heavy metal release was reduced to below Chinese National standard. Data analysis using Fourier-transform infrared spectra data and model calculation using visual MINTEQ program indicated that humic substance strongly affect mobility of organic fractions of heavy metals in methanogenic landfill. Total heavy metal leached can be reduced by early establishment of methanogenic phase. This paper reveal finding which confirm heavy metal leaching when subject to organic acid create by early stage of biological degradation in landfill. (Xian Qu *et al.*, 2007).

L. Borzacconi investigated hydrolysis constant and volatile fatty acid inhibition in acidogenic phase of MSW anaerobic degradation. Result include interpretation of VFA/COD ratio result which was use as indication of acidogenesis process when methanogenic phase is not been reach. High organic content create undiminished ratio of VFA/COD which indicated that there were inhibition of acitogenesis due to the accumulation of undissociated VFA. Due to this, growth of methanogenic organism was inhibited by extremely low pH cause by organic acid accumulation. (Borzacconi *et al.*, 1997)

Bozkurt investigated long-term process in industrial and municipal waste deposits and its effect on toxic metal leaching. Simulation by using mathematical model varies different longevity, function of cover, different air/water intrusion rate, binding capacity of sulfide and humic substances. The model start at humic phase, which is phase after methane generation is completed. Research finding indicate that long-term heavy metal leaching potential were controlled by characteristic of heavy metal and pH buffering reactivity. Result conclude that remobilization of heavy metal is not expect for thousands of years (Bozkurt *et al.*, 2000)

I. Maharaj and P. Elefsiniotis investigated role of hydraulic retention time and low temperature on acid-phase anaerobic digestion of municipal and industrial wastewater. All parameters relate to VFA and COD production were significantly higher in industrial-municipal reactor than municipal-only reactor. Result reveal high VFA/COD ratio of 0.8 -1 indicate that hydrolysis was the rate limiting step. (Maharaj and Elefsiniotis, 2000).

6. Analytical Method: USEPA 1684

Total solid, Volatile Solid, Fixed solid and Moisture can be determine using method 1684 by USEPA. The method are as following figure;

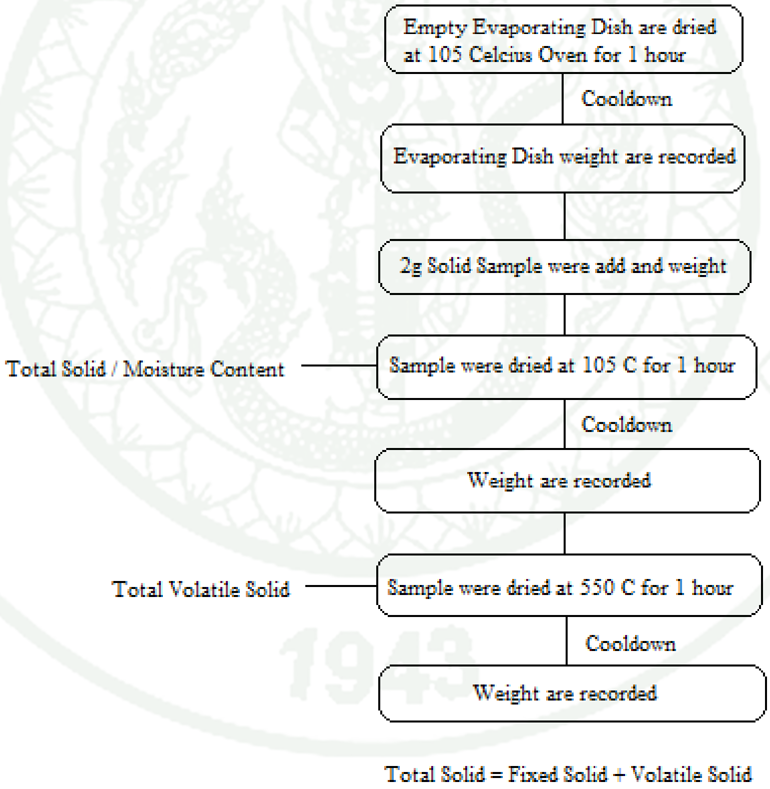


Figure 2 USEPA Method 1684 TS,VS, FS and Moisture content determination

Interferences can occurred from weight losses due to volatilization of organic matter due to extent period of cooling and weight gain from air moisture get absorbed by samples due to surrounding. These can be minimized time the desiccators is open and avoid cooling overnight.

7. Analytical Method: Total Organic Carbon

Total organic carbon content need to be measured since it is the objective of this thesis to investigate amount of organic carbon that has been used by microorganism during reactor's operation. Total organic carbon can be determined by using high temperature combustion method (Standard Method for the Examination of Water and Wastewater, Method 5310B, 2005).

In principle, TOC analyzer operate base on infrared spectroscopy. Nearly all organic chemical compound show marked selective absorption in infrared region. (Sawyer *et al.*, 2003). Infrared spectra can identify particular atomic grouping in an unknown molecule. Because complexity of infrared spectra it is unlikely that two different compound will have identical spectrogram curve. However when many materials are present in solution, sample separation procedure is require isolating compound of interest in order to minimize interferences between each compound individual spectra. However, sample need to be injected in liquid form.

Shimadzu's total organic carbon analyzer with solid sampling module (TOC-Vsh/SSM) allow user to analyze total organic carbon directly from solid sample. The result will be displayed as micro-gram of carbon within sample which can be further calculated as percentage from sample which weight with 3 digits balance.

According to figure 3, sample will need to be processed in two consecutive steps to obtain total organic carbon reading. Firstly empty boat (sample carrier) must be burnt inside 900 degree Celsius furnace to get rid of any external carbon contamination. When sample entered furnace carbon dioxide emission from burning of sample will be measured to determined total carbon in the sample. Carbon dioxide formed is transport to detector via stream and measure by infrared detector. The amount of carbon dioxide will be directly proportional to concentration of total carbon material in sample. Secondly sample need to be acidified with hydrochloric acid to remove organic carbon. Sample then burnt in 200 degree Celsius Furnace (which design for analyze inorganic carbon). Product of combustion gave the amount of inorganic carbon within sample.

Total organic carbon then obtained by calculate from result of total carbon minus inorganic carbon. Figure 5 show process of determine total organic carbon using Shimadzu's TOC-Vsh- SSM.

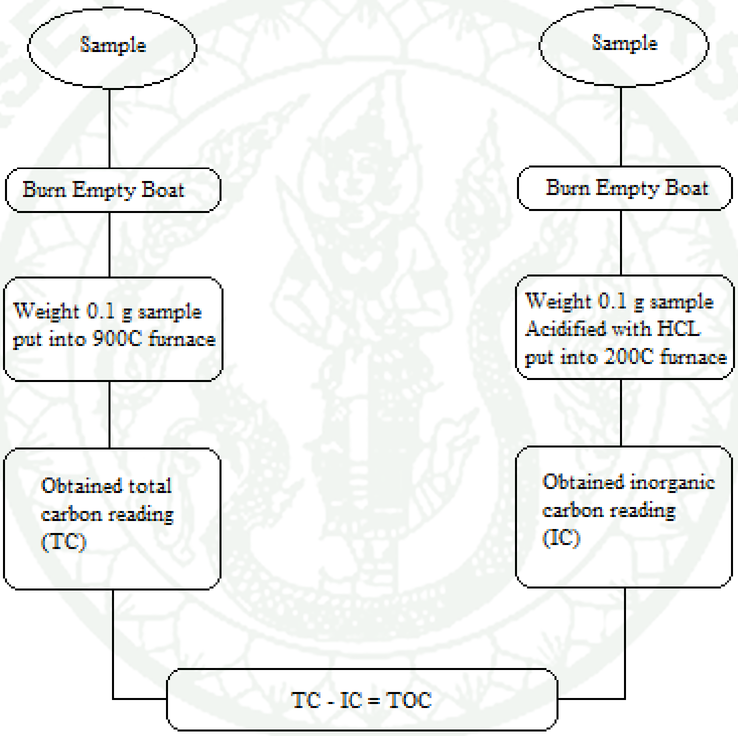


Figure 3 Total organic carbon analytical procedures using TOC-Vsh / SSM

8. Analytical Method: Volatile Fatty Acid

Volatile fatty acid and bicarbonate measurement are important to assess anaerobic degradation process stability. The anaerobic digester consists of train of biological activities; acidogenesis, acetogenesis and methanogenesis. CO_2 and VFA are produced and consumed by acetotrophic methanogenesis which utilize VFA and hydrogenotrophic methanogenesis which utilize CO_2 and H_2. However if VFA level start to accumulate while CO_2 continuously stripped (causing pH decrease), the biological activity will be inhabit. In other word, methane organism fail to keep pace with fermentative and acid producing organism. Volatile fatty acid can be measure by using several method; 1. Distillation method (standard method 5560C) 2. Gas chromatography 3. Column partition chromatographic method and 4. Titration method

8.1 Distillation method

The direct distillation method is commonly used for routine measurement of volatile acid because of its rapid and sufficiently accurate for practical purpose. This method use principle that all low-molecular weight fatty acid have significant vapor pressure at 100 C° so the sample's distillate will contain most of those acids. However, at pH range between 6.5 and 7.5 which is normal for anaerobic reactor will cause organic acid to remain in ionic form and cannot be distilled.(Sawyer *et al.*, 2003). Therefore addition of strong non-volatile acid such as sulfuric acid to reduce pH to below 1 must be done in order to convert organic acid to un-ionized form so it can be distilled.

The distillation rate is an important factor and should be carefully control. Low rate of distillation will cause fractionation at neck of the flask and volatile acid will not carry over to distillate. Care also must be taken to stop distillation process before sulfuric acid in flask become concentrated and cause decomposition of other organic material and gave inaccurate result. Distilled acid then are measure quantitatively by titration with standardized NaOH solution to phenolphthalein end point. Approximately 70% of volatile acid are captured and this will be taken into account in calculating volatile acid present. (Standard Method For The Examination of Water and Wastewater, Method 5560C, 2005)

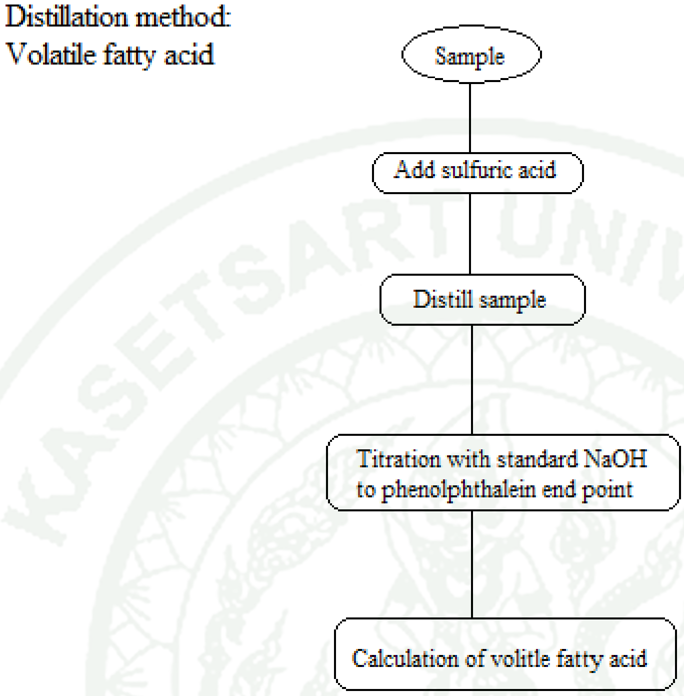


Figure 4 Distillation method for volatile fatty acid analytical procedures

8.2 Gas chromatography method

Gas chromatography can also be use to measure amount of volatile acid present. Its mechanism involve gas cylinder contain a carrier gas such hydrogen, helium or nitrogen and inject sample which will immediately in gas phase by flash-evaporation method. Since gas travel at different rate so they exit the column at different time, The machine measure travel time each type of gas either physical or chemical mean. The responds of detector through electrical recorder create chromatogram. Peak of chromatogram represent specific compound with same rate of movement through column while area under peak is proportional to concentration of compound in the sample. Figure 5 show operation of gas chromatograph.

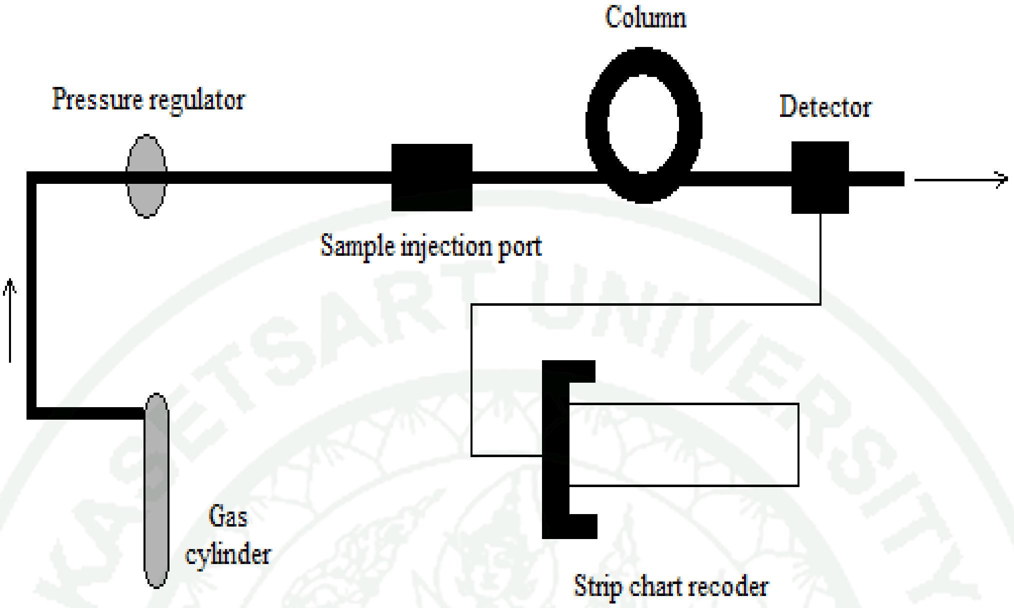


Figure 5 Schematic diagram of a gas chromatograph

Column partition chromatographic method involve 2 solvents, One is fixed on solid adsorbent and another is mobile solvent which carries the material to be separate through the column. When they are moving through the column, they produce differential migration of various materials. More soluble material in moving phase will emerge from column first. This principle is applicable for gas, liquid and ion chromatography (Sawyer *et al.*, 2003). There are 2 type of detector used by GC, Thermal conductivity detector (TCD) and Flame ionization detector (FID). TCD respond to all pure substance unlink FID which only respond to carbon hydrogen compound. TCD testing method is non-destructive unlike FID which performed destructive testing of sample.

In order to analyze sample, suspend solid are first removed by filtration or centrifugation then sample is acidified with strong inorganic acid (sulfuric) to convert volatile acid from ionized form to unionized form. Given quantity of chloroform-butanol mixture is pass through column and will selectively carry unionize volatile acid because they are more soluble in this mixture than stationary phase. However it is important to make sure sufficient mobile solvent is added to carry all volatile acid but if too much, inorganic acids are carried through. Organic solution is then titrate by sodium hydroxide in methanol solution to phenolphthalein endpoint.

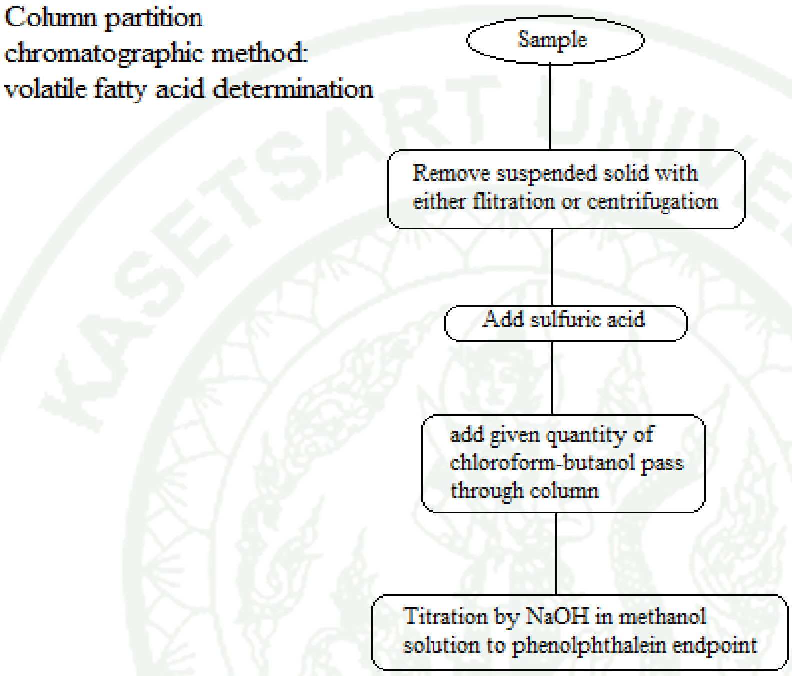


Figure 6 Column partition chromatographic method: volatile fatty acid determination

8.3 Titration method

Titration method is the easiest way of measure amount of volatile fatty acid in leachate sample. Following Standard method of water and waste water examination, using sulfuric acid and sodium hydroxide to adjust pH. Then amount of volatile fatty acid presence in sample can be calculated. The process are shown in figure 7 below;

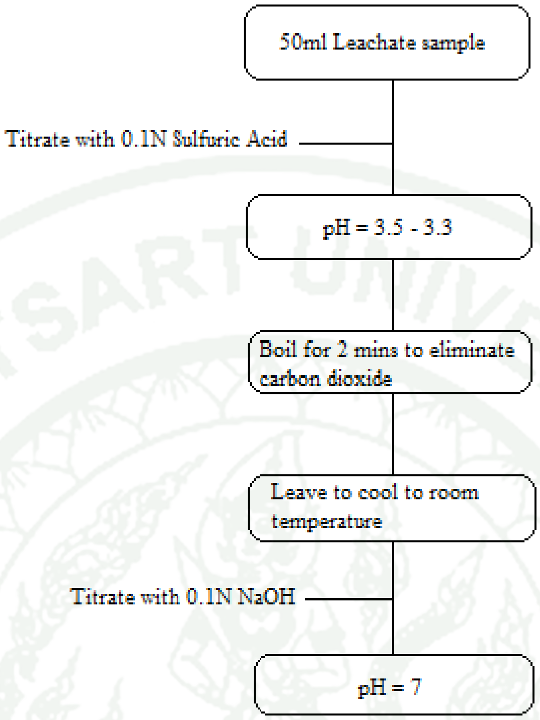


Figure 7 Titration method: volatile fatty acid determination

9. Analytical Method 5220C: COD determination

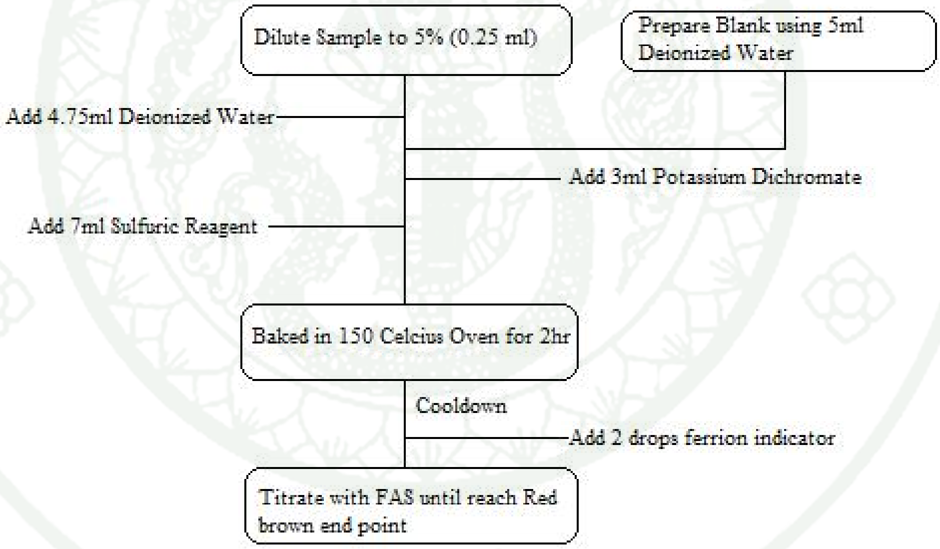
Chemical oxygen demand usually being used to indirectly measure amount of organic compounds in water. It is commonly used as indicator of water quality because its process is less time consuming than biological oxygen demand (BOD) determination. In general case BOD is 60% of COD, therefore COD can be use roughly as a quick assessment of water quality. Theoretically it is the amount of oxygen required to fully oxidized organic compound with aid of strong oxidizing agent (potassium dichromate) under acidic condition (concentrated sulfuric acid).

In order to perform COD determination of leachate sample, following chemical must be prepared according to standard method for water and wastewater examination method 5520C;

1. 0.25N Potassium Dichromate
2. Sulfuric reagent (Ag_2SO_4 + Concentrated Sulfuric Acid)

3. 0.25N Ferrous Ammonium Sulfate (FAS)
4. Ferroin Indicator

However, Dilution factor of sample must be determined first. If sample is too strong, the amount of Potassium Dichromate added might not be sufficient to oxidized all organic compound within sample resulting green color. If sample is too dilute, different between blank and sample might be too little and calculation will be wrong. Figure 8 show process and calculation require to determine chemical oxygen demand using prepared reagent.



$$\text{COD} = \frac{8000\,(\text{FAS titrated Blank} - \text{FAS titrated Sample}) \times \text{FAS normality}}{\text{Sample} \times \text{Dilution factor}}$$

Figure 8 Method 5220C Close reflux method for COD

10. Analytical Method: Metal analysis using AAS

Atomic absorption spectrophotometry provides accurate quantitative analyses for metals in water, sediments, soils or rocks. (Samples are analyzed in solution form, so solid samples must be leached or dissolved prior to analysis.) Atomic absorption units have four basic parts: interchangeable lamps that emit light with element-specific wavelengths, a sample aspirator, a flame or furnace apparatus for volatilizing the sample, and a photon detector. In order to analyze for any given element, a lamp is chosen that produces a wavelength of light that is absorbed by that element.

Figure 9 show operation of atomic absorption spectrophotometer. Firstly the light source with wavelength which is readily absorbed by element to be measure is directed through flame. Intensity measurement is made without sample and then with sample introduced into flame. Differences of intensity observe will measure of concentration of the target element. Limitation of this method is that different light source must be used for each element. Fortunately, hollow cathode lamps can be use for most naturally occurring elements.(Sawyer *et al.*, 2003).

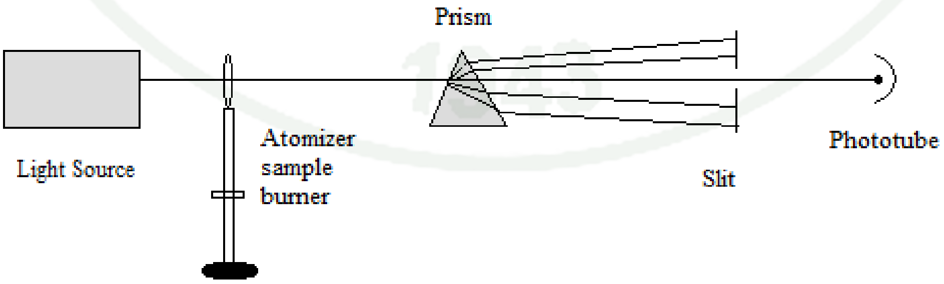


Figure 9 Schematic diagram of Atomic absorption spectrophotometer
Source: Sawyer *et al.*, (2003)

Sample solutions are aspirated into the flame. If any ions of the given element are present in the flame, they will absorb light produced by the lamp before it reaches the detector. The amount of light absorbed depends on the amount of the element present in the sample. Absorbance values for unknown samples are compared to calibration curves prepared. Prior to injection to Atomic absorption spectrophotometer sample must be prepare following standard procedure for digesting samples (Method 3051A; solid, Method 3030E; liquid); Nitric acid and hydrochloric acid were use as reagent. Solid particle within digested sample must be eliminate using combination of centrifugation and membrane filter. Sample must be adjust to have pH of 2 by adding nitric acid after filtration, before being analysis by atomic absorption spectrophotometer.

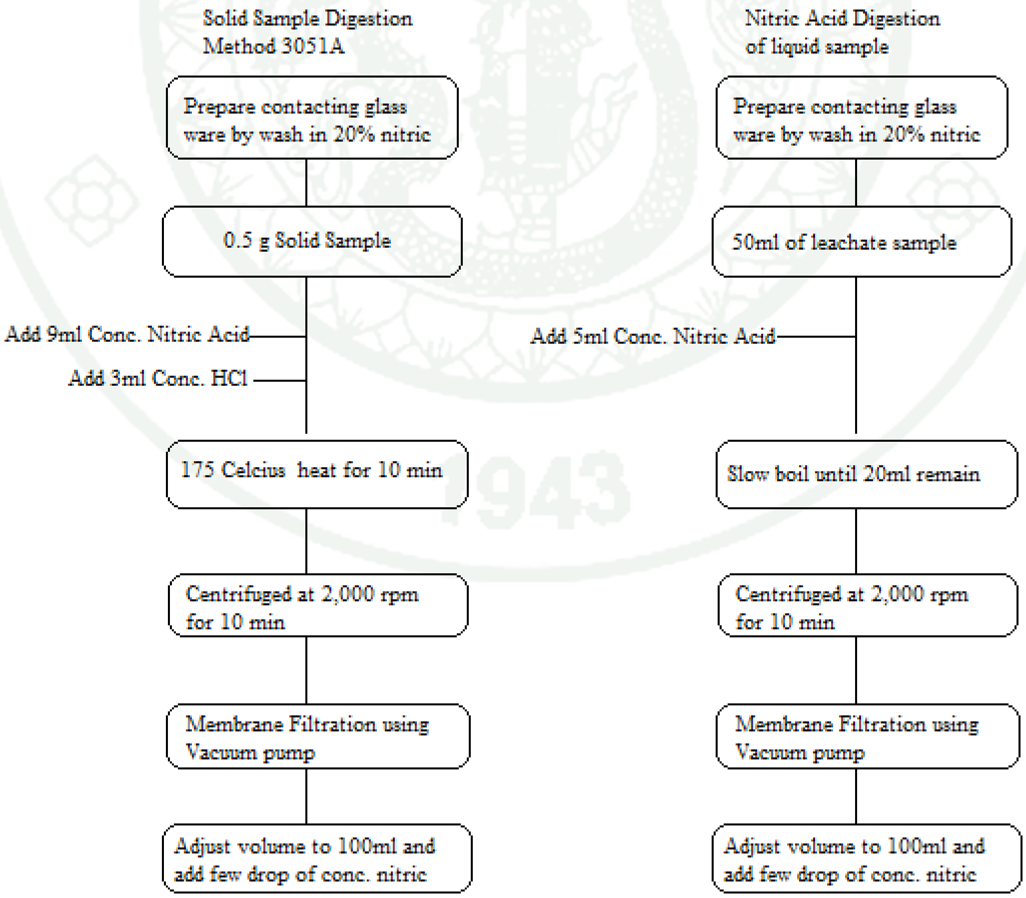


Figure 10 Solid (3051A) and liquid (3030E) sample preparation prior AA analysis

MATERIALS AND METHODS

Materials

Materials and equipment used for conducting this research were listed below.

1. 8” PVC cylinder reactor with 1m height
2. Perforated plastic sheet
3. Metal frame for supporting 3 column
4. Spray nozzle
5. Bronze valve with filter inside
6. 250 ml plastic beaker
7. Pump (Laboratory peristaltic pump) and 220V pump power supply
8. Rubber tube

Laboratory equipments used for analyses experimental results were listed below.

1. pH probe
2. Atomic Absorption Spectrophotometer
3. Gas chromatography (Agilent 6890) with TCD detector
4. Shimadzu Total Organic Carbon analyzer (TOC-Vsh) with Solid sampling module (SSM)

Methods

Three phases of laboratory experiments were conducted at the environmental engineering laboratory, Kasetsart University. Details of the experiments are presented below.

1. Hazardous Waste Material Preparation

Hazardous waste sample were taken from the waste treatment plant at Samaedum which is operated by GENCO company limited. The waste samples were collected from the stabilized waste including:

1. Sludge from physical – chemical treatment for electroplating industry wastewater. This sludge contains high amount of heavy metals and toxicity

2. Sludge from physical – chemical treatment for dyeing wastewater. This sludge contains high amount of solids and COD.

The hazardous waste samples were mixed with lime to reduced toxicity and then solidified by cement to reduced the pollutant mobility before burring in a secured landfill.

2. Laboratory scale simulating landfill reactor design

Three identical simulating landfill reactor were constructed with following specification; single pass PVC reactor without leachate recycle has diameter of 0.23 m (8 inch) and height of 1 m (figure.11). The reactor was equipped with 2 inlet port at the top lid for rainwater addition and gas sampling. A leachate sampling port was placed at the bottom of the reactor. Leachate collection system consisted of pea gravel layer to eliminate large solid particle to escape with leachate flow to the leachate sampling port. The reactor was protected from the sunlight and operated at the room temperature (34 Degree Celsius). Reactor was insulated to prevent heat loss and accelerate biological reaction.

Deionized water was added to the reactor representing the rainfall. The amount of rainfall added was calculated following monthly rainfall data in 30 years as shown in table 2.

Table 2 Rachaburi's average in monthly rainfall data

Month	Total Rainwater (mm)[a]	Rainy day (day)
January	3	1
February	14.5	2
Marsh	70.9	11
April	48.3	6
May	147.7	16
June	125.2	12
July	190.5	13
August	170.7	17
September	277.5	17
October	231.9	13
November	22.9	5
December	0	0
Maximum wet season rainfall (mm) and rainy day	870.6	60
1st experiment month total rainfall amount (mm) and (l) convert using *, ** to surface area	14.65 mm per day for 13 days	[b]2.43 L per month and [d]0.187 L each addition for 13 day
2nd experiment month total	10.04 mm per day for 17 days	1.67 L per month and 0.0982 L each addition for 17 days
3rd experiment month total	16.32 mm per day for 17 days	2.709 L per month and 0.1594 L each addition for 17 days

The periods of experiments were taken for 3 months for each phase, therefore only wet season with maximum amount of rainfall was taken into consideration. The rainwater distribution system consisted of nozzle connecting with pump. The pump then connected with water tank and 220V power supply according to figure 11.

Note [a]1mm of rainfall = 1L per M2

[b]from (0.166c/1)x14.65 mm =2.43 L convert to ratio of reactor's cross section

[c]Cross section area of each reactor = 0.166 m2

[d]2.43 / number of rainy day for this month

Data Source : Thai Meteorological Department (www.tmd.go.th)

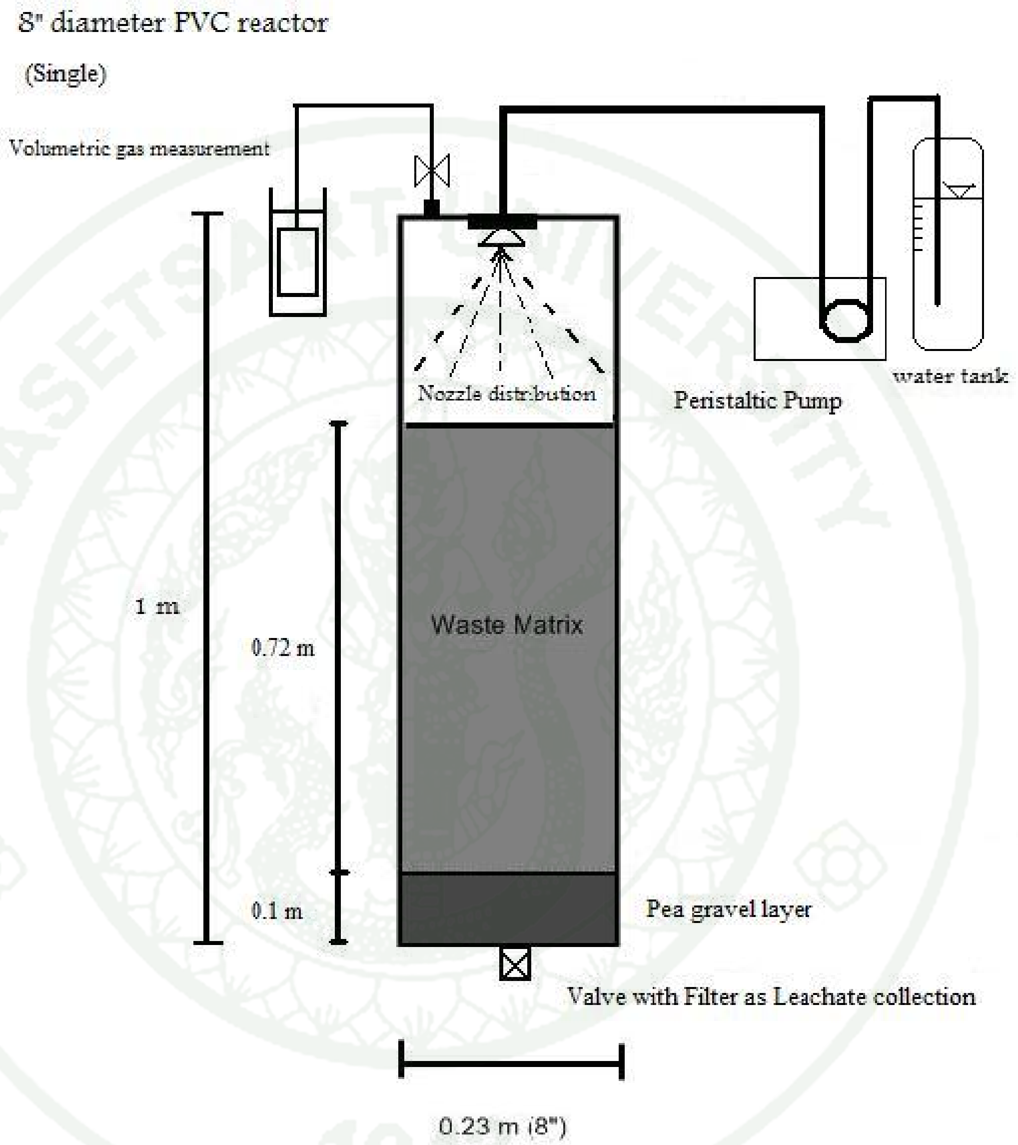


Figure 11 Configuration of single pass landfill reactor

3. Phase 1: The effect of volatile fatty acid on heavy metal leaching

The first phase was a batch experiment that was used to study the effect of variation of volatile fatty acids on heavy metal leaching. In this experiment, the stabilized hazardous waste samples from the secured landfill were added with acetic acid which represented the product from acidogenic bacteria activity. Ten grams of each sample were added in the 250 ml Erlenmeyer flask with 100ml of acetic acid following the Toxicity Characteristic Leaching Procedure (TCLP), and it then was shaken at 30 rpm for 18 hours. The extracted samples were separated from solid samples. Then, there samples were digested under acid condition and analyzed by the Atomic Absorption Spectrometer to determine the heavy metal concentrations. The heavy metals such as Cr, Ni, Pb and Cd were analyzed. Figure 12 shows the experimental procedure of the first phase.

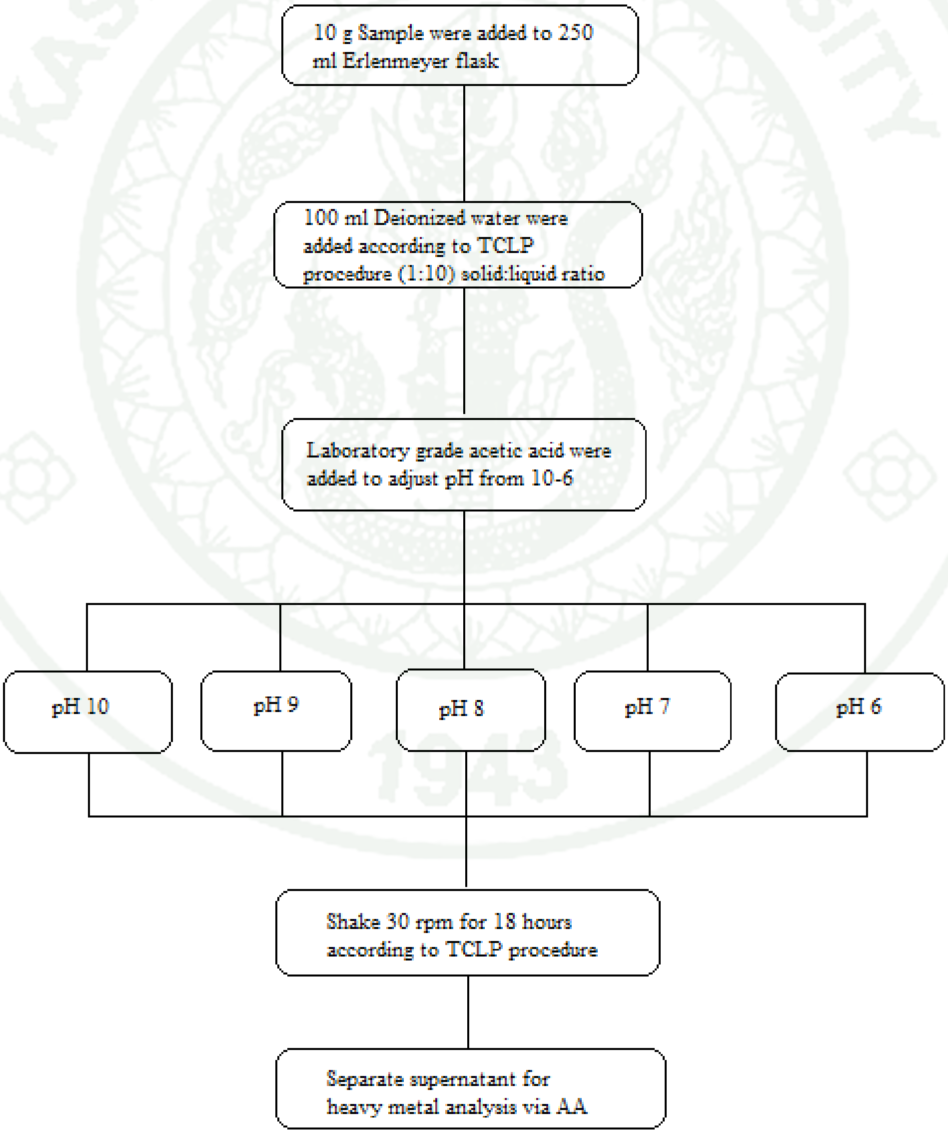


Figure 12 Phase 1 methodology

4. Phase 2: The Change of organic matter in the landfill reactor

In the second phase, three landfill reactors were design to determine the degradation of stabilized hazardous waste sample from the Ratchaburi secured landfill. The experimental procedure are shown in figure 13 the details of experiments including:

4.1 Waste matrix preparation

The waste matrix in this experiment were prepared from the stabilized hazardous waste collected from the Ratchaburi hazardous waste landfill. The waste matrix was put in the landfill reactor, with the total weight of 17.1 kilograms (23.29 Litre) at the height of 73 cm.

4.2 Sampling and analytical methods (phase 2)

Leachate from the reactor was sampling on regular basis to determine the heavy metal concentration. Leachate sample was collected from bottom sampling port and then was analyzed for pH, VFA and heavy metal content such as Cd and Cr which are considered as the most toxic pollutant. The measurement pH was performed following the Standard Method for Examination of Water and Wastewater. Heavy metals were analyzed by the atomic absorption spectrophotometer. In addition, volatile fatty acid was analyzed by titration method according to the Standard Method for Examination of Water and Wastewater. Throughout reactors operation, gas generation data were collected by water-displacement volumetric gas analysis. Sludge sample were analyzed at beginning and the end of experiment to compare different interested parameter such as Total organic carbon (TOC), heavy metal content and inorganic component.

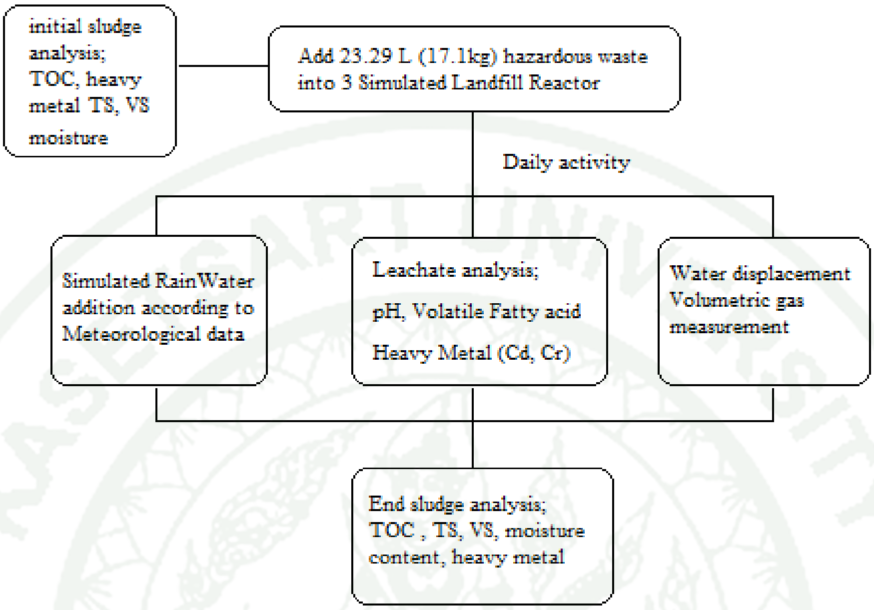


Figure 13 Phase 2 methodology

After total organic carbon analysis (TOC) and metal analysis of initial sample from secured landfill completed, Phase 1 and 2 experiments were conducted simultaneously.

5. Phase 3: Landfill reactor operation to investigate mass balance of system

Phase III experiment were conducted to find necessary data to construct theoretical mass balance of the simulated landfill system. Where additional parameters such as total dissolve solid (TDS) and chemical oxygen demand (COD) are also constantly monitored throughout reactors operation. Rainwater addition quantity has been changed to be constant at maximum month (month 3 on table 2) in order to determine maximum leaching of contaminant. Gas production, pH and Volatile fatty acid are still being monitored throughout reactor operation period of 90 days. Each reactor were packed with 14.9 kg of hazardous waste sludge. Initial sample for each reactor has been taken and analyzed for total organic carbon for several replications in order to generate average percentage of organic carbon contain within each reactor.

5.1 Sampling and analytical methods (phase 3)

In this phase, leachate sample were taken regularly to analyzed for Volatile fatty acid (VFA) and pH using same analytical methods as previous phase. Additionally total dissolved solid (TDS) and chemical oxygen demand (COD) were also monitored in order to determine mass flow out of system along with leachate sample. Gas generation was monitored using water-displacement volumetric gas analysis equipment same as previous phase. Additionally gas sample was taken from each reactor to be analyzed by Agilent's model 6890 gas chromatography for breakdown of gas composition. Initial and end sludge sample from each reactor were taken to analyzed for total organic carbon (TOC) content using Shimazu's total organic carbon analyzer with solid sampling module (TOC-Vsh/SSM).

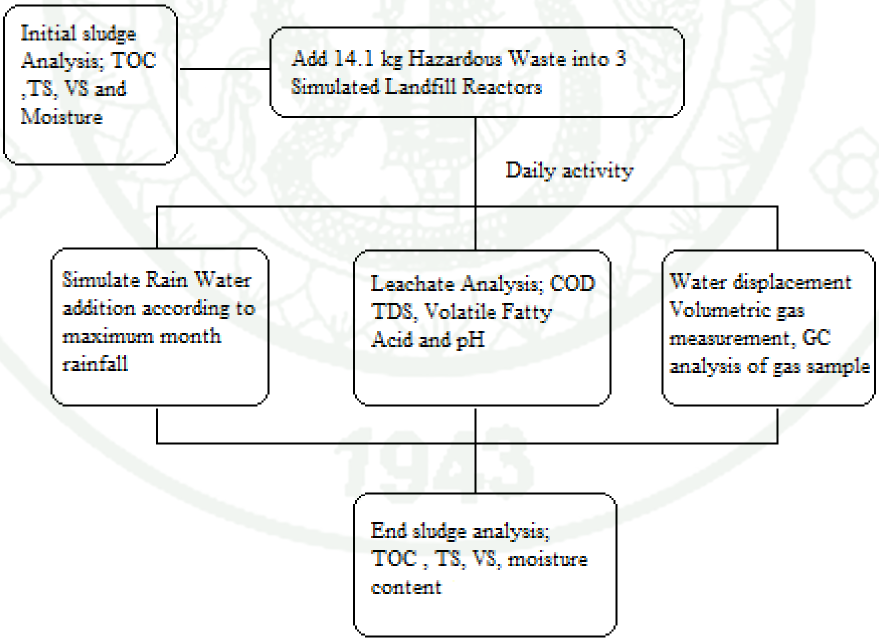


Figure 14 Phase 3 methodology

RESULTS AND DISCUSSION

Results

Results were divided into 3 phases of experiment, Phase 1 was laboratory scale experiment while phase 2 and 3 involved simulated landfill reactor operation.

1. Phase 1 and 2 Hazardous Waste Material Characteristics

Prior to phase 1 and 2 experiment, sludge were taken for analyze for total solid, fixed solid, volatile solid and moisture content following USEPA method 1684. Total carbon, total inorganic carbon and total organic carbon of samples were analyze with Shimadzu's total organic carbon analyzer with solid sampling module following combustion method 5310B according to Standard method.

Table 3 Phase 1 & 2 Waste Characteristics prior to reactor operation

Total Solid	97.8348%
Fixed Solid	99.4953%
Volatile Solid	0.5047%
Moisture Content	2.1652%
Total Carbon	6.08%
Total Inorganic Carbon	0.91%
Total Organic Carbon	5.17%
Total Organic Carbon in Reactors	0.88 kg from 17.1 kg
Texture	Brown Clay-like

2. Leaching Test

As acetic acid was directly added to the stabilized hazardous waste mixed with de-ionized water in 1:10 solid/liquid ratio, pH was determined. In this experiment the amount of acetic acid shown in table 4 was added until pH changed from initial pH to 6. It was found that buffer reaction took place between pH 7 to 6 due to double amount added to reduce pH. As pH was reduced, it was found the concentrations of heavy metals from the leachate increased as shown in figure 15. This follow hypothesis which heavy metals dissolution of from the stabilized waste matrix cause by acetic acid which is major by product of biological degradation process.

Table 4 Amount of 0.25N acetic acid added (ml)

	pH 10	pH 9	pH 8	pH 7	pH 6
Sample Initial pH 11.72	10.2	20.5	30.1	40.1	56.9
Sample Initial pH 12.02	13.2	21.9	30.6	41.6	59.2

Maximum concentration of nickel (Ni) leached was at 2.5 mg/l at pH 7. Maximum concentration of lead (Pb) leached was at 0.8 mg/l at pH . Maximum concentration of chromium (Cr) leached was at 10.56 mg/l at pH 7 and lastly maximum concentration of cadmium (Cd) leached was at 0.042 mg/L at pH

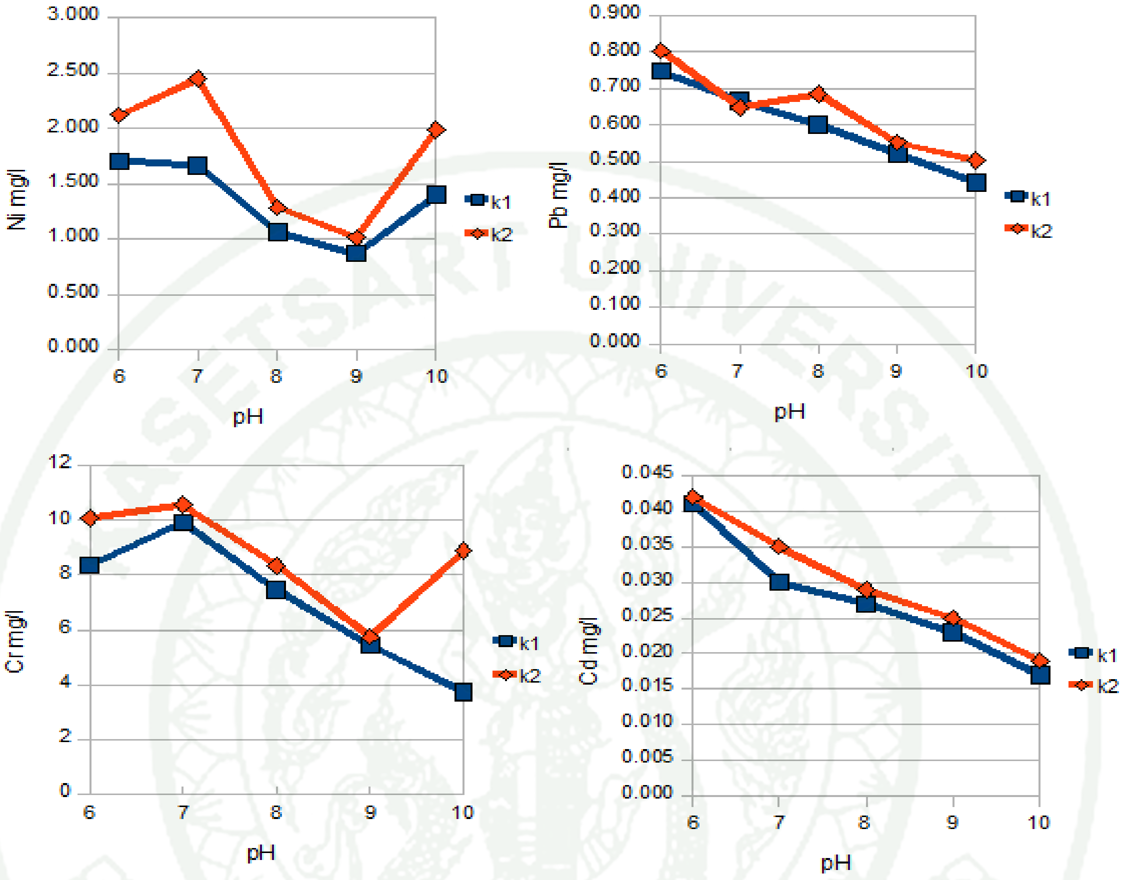


Figure 15 Leaching test result Heavy Metal vs pH

From this experiment phase, it was found that the change of pH did not sharply occur although acetic acid was added due to the lime stabilization buffer capability. Thus, the neutralization of acetic acid by lime is still a major process to maintain the pH level. However, as the amount of acetic acid was increasingly added over the loading capacity of stabilizing agent, pH was rapidly decreased.

3. Phase 2: Microbial Activity Performance

During the simulated landfill reactor operation, the simulated rainfall condition was calculated from actual landfill site's meteorological data. Season with highest precipitation was chosen to determine maximum leaching condition. Three landfill reactors were operated with the same condition. To show that the microbial activity occurred in the stabilized hazardous waste landfill, VFA production, pH value and gas production were determined. Also, the amounts of heavy metals were determined from the leachate. Volatile solids and total solid portion of stabilized waste were determined using standard method.

3.1 pH of leachate

The initial pH were 12.32, 11.28, 10.5 for reactor 1,2 and 3 respectively. Figure 17 shows pH value of the leachate which remained nearly constant at 11-12 due to neutralization of lime stabilized sludge within reactor. The pH of feed water ranged from 5-6 was simulated following acidic rain condition. This water added did not affect the pH of the leachate. Also, the production of VFA found in the system was not related to pH reduction in the leachate this occurred due to buffer capacity of waste body. Thus, the neutralization plays an important role in maintaining pH level for the stabilized waste in the landfill.

3.2 Volatile fatty acid concentration in leachate

The concentration of volatile fatty acid in the leachate was determined to indicate the microbial activity occurred in the landfill reactors. Figure 16 show volatile fatty acid concentration in leachate from reactor 1,2,and 3, respectively.

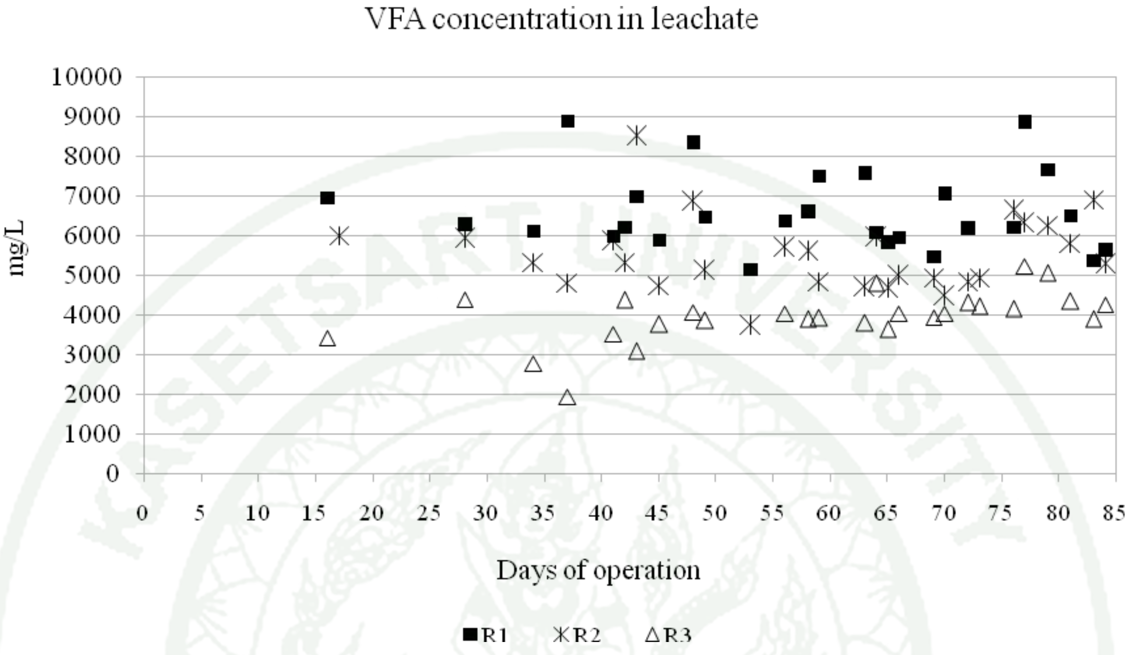


Figure 16 VFA concentration in leachate during phase 2 experiment

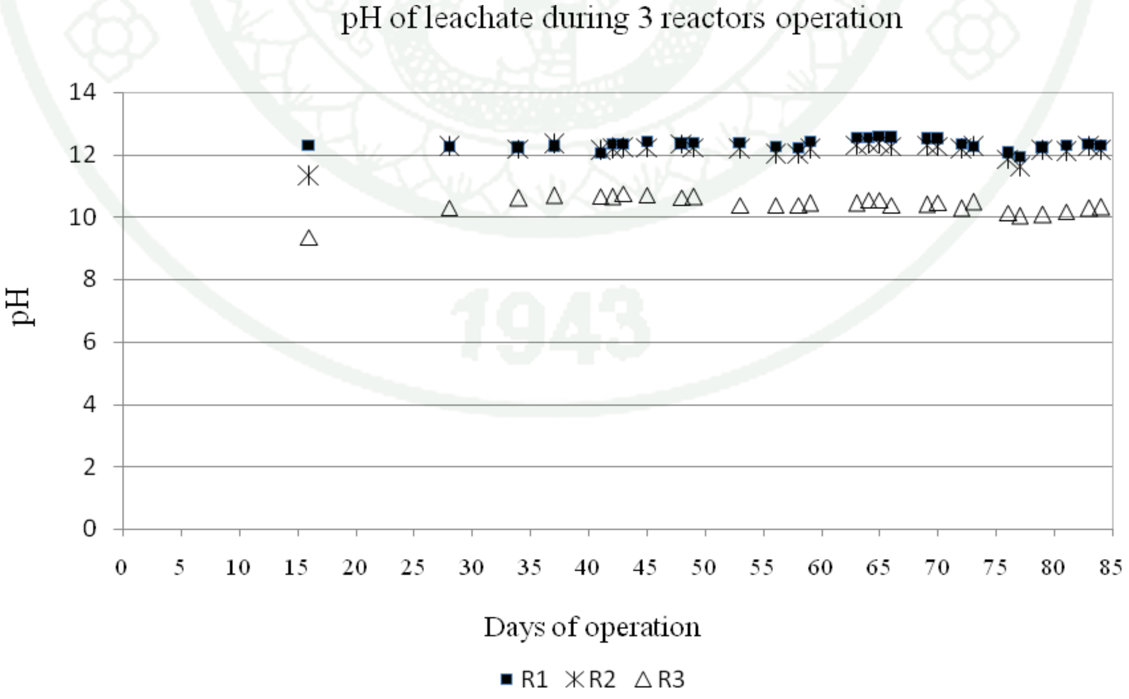


Figure 17 pH of leachate during phase 2 experiment

It was found that the average concentration of volatile fatty acid in reactor 1 was 6,667 mg/l (minimum value of 5,160 mg/l and maximum value of 8,910 mg/l). In reactor 2, the average concentration of VFA was about 5,464 mg/l (minimum value of 3,750 mg/l and maximum value of 8,520 mg/l). Reactor 3 had lowest overall VFA concentration with average value of 3,890 mg/l (minimum value of 1,950 mg/l and maximum value of 5,235 mg/l). Compared to acidogenesis phase of municipal landfill which ranged between 7,500 – 15,000 mg/l (L. Borzacconi et al., 1997). This indicated that microbial activity has occurred inside landfill reactors. After 3 months, it was found that VFA produced was at maximum loading of 0.21 kg from 23.29 L total.

3.3 Gas produced from simulated landfill reactor

Figure 18 shows gas production rates from these three reactors which were slightly different but yet the overall gas production quantities were similar. During first 24 days, only reactor 1 has produced 250 ml of gas while the gas productions from the reactor 2 and 3 were very low. From day 28 to day 50 there is a slight increase in overall gas volume from 50 to 500 ml and remain constantly from day 50 to day 65. After day 69, gas production increased sharply from 1000 ml to 2000 ml. This indicated that the acclimatization of microorganism in the stabilized hazardous waste was about 65 days. This was also approved by the gas production accumulation shown in figure 21.

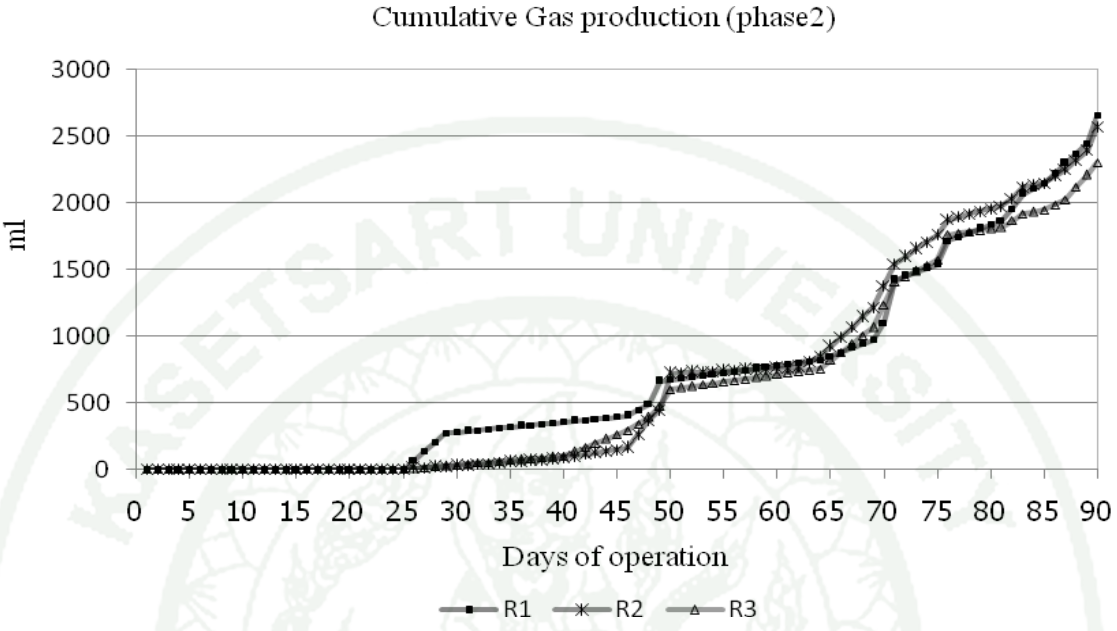


Figure 18 Cumulative gas production from phase 2 experiment

The gas emitted from the reactor 1,2 and 3 were 2655 ml, 2570 ml and 2300 ml respectively.

3.4 Cr and Cd concentration in leachate

The variation of heavy metals from the leachate was investigated and showed in the figure 19. Chromium (Cr) and cadmium (Cd) were analyzed by using atomic absorption spectrophotometer twice a month. The results showed that the concentration of Cr rapidly increased to 1.528 mg/l, 1.103 mg/l and 0.430 mg/l for reactor 1,2 and 3 respectively on the day 44. While the concentration of Cd in the leachate was slowly increased in linear trend for 3 reactors, as accumulation of volatile fatty acid in the system increased. This spike behavior of graph is best explain by error of data point. However, the leaching of Cr and Cd were confirmed.

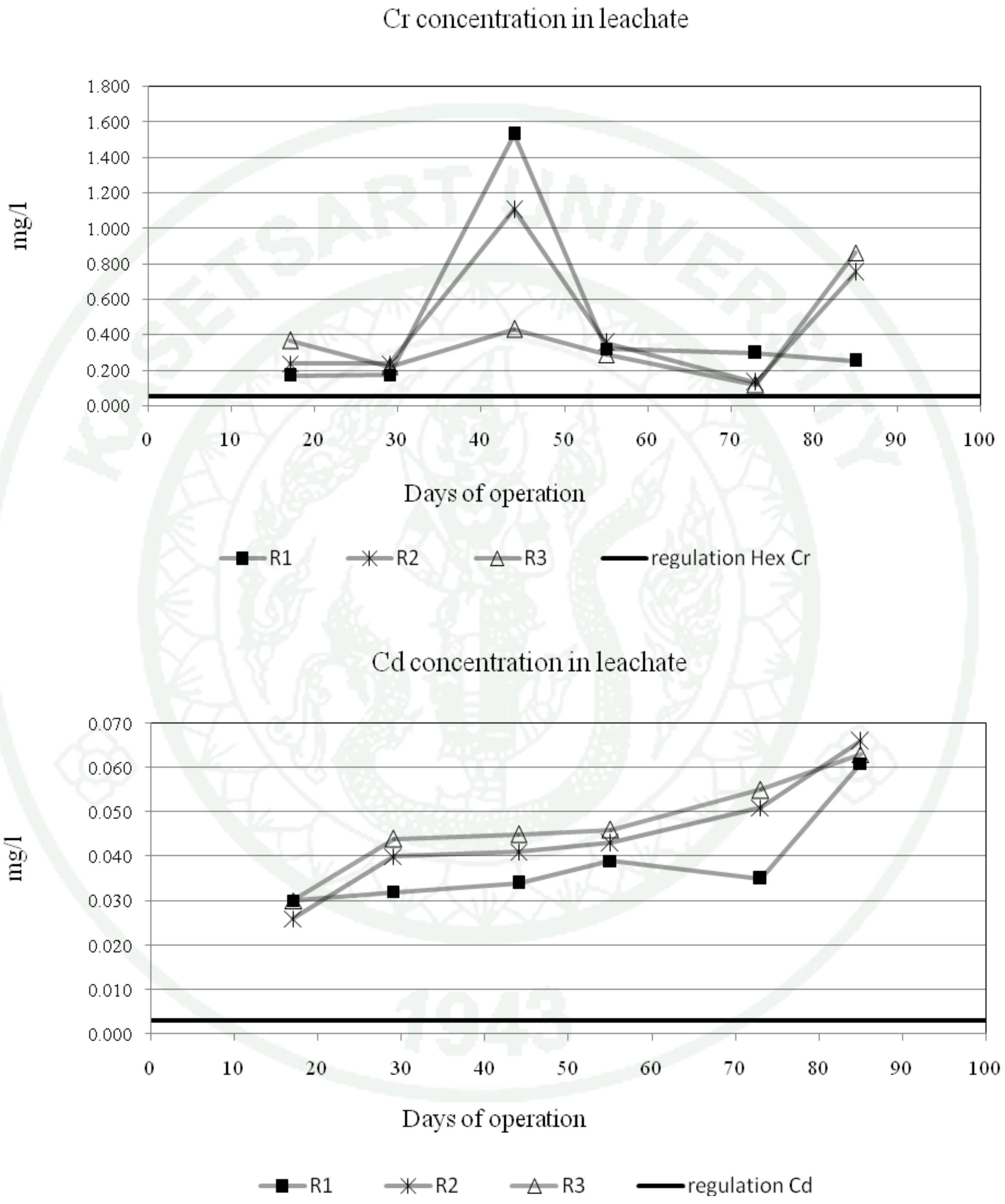


Figure 19 Cr and Cd leaching during phase 2 experiment

The transformation of an initial TOC to be VFA, methane and carbon dioxide gas, and TOC remaining was investigated as shown in figure 20.

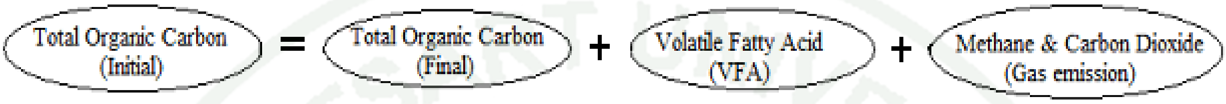


Figure 20 Mass Balance of the system concerning TOC transformation

From table 5, it was found the initial TOC (0.88 kg) from the stabilized waste was reduced to 0.62 kg, 0.63 kg and 0.73 kg from the reactor 1,2 and 3, respectively. Total organic carbon had been reduce by 0.262 kg, 0.255 kg and 0.147 kg respectively. Total organic carbon content of an initial sludge sample and end sludge sample were determined in table 4 using Shimadzu's total organic carbon (TOC) analyzer with solid sampling module.

Table 5 Phase 2: Waste Characteristics after reactor operation

	Reactor 1	Reactor 2	Reactor 3
Total Solid	98.46%	97.58%	97.93%
Fixed Solid	99.77%	99.63%	99.70%
Volatile Solid	0.23%	0.37%	0.30%
Moisture Content	1.54%	2.42%	2.07%
Total Carbon	4.65%	4.57%	5.12%
Total Inorganic Carbon	1.04%	0.92%	0.83%
Total Organic Carbon	3.61%	3.66%	4.28%
Total Organic Carbon in Reactor	0.62 kg	0.63 kg	0.73 kg
Change in Total Organic Carbon	- 0.262 kg	- 0.255 kg	- 0.147 kg

Reduction in total organic carbon was due to the microbial activity. The result is directly correlate to several microbial performance indicator such as volatile fatty acid production, gas production and chromium leaching. Biological reaction occurred most in reactor 1 indicated by highest gas production and highest level of volatile fatty acid. However, Total Organic Carbon (TOC) mass balance from the stabilized waste as in figure 19 was further investigated in phase 3 reactors operation.

4. Phase 3: Results from reactors operation

Main objective of phase 3 experiment was to determined mass balance for carbon content in the system. Initial carbon content were reduced by both biological activities which included volatile fatty acid production and gas production or simply leaching out with leachate sample in form of chemical oxygen demand (COD) or total dissolved solid (TDS).

Table 6 Phase 3 Hazardous Waste Material Characteristics prior to experiment

	Reactor 1	Reactor 2	Reactor 3
Total Solid	97.52%	96.86%	97.32%
Fixed Solid	99.69%	99.85%	99.47%
Volatile Solid	0.31%	0.15%	0.53%
Moisture Content	2.48%	3.14%	2.68%
Total Carbon	2.88%	3.50%	4.50%
Total Inorganic Carbon	0.42%	0.43%	0.52%
Total Organic Carbon	2.46%	3.08%	3.98%
Total Organic Carbon in Reactor	0.3661 kg	0.4582 kg	0.5925 kg

4.1 pH of leachate

During phase 3 simulated landfill reactors operation, simulated rainfall addition were changed to be constant throughout experiment period at month 3 in table 2. Initial pH were 7.07, 7.41 and 7.01 respectively this is greatly different with phase 2 hazardous waste due to different batch of sample.

According to figure 21, pH value of the leachate from 3 reactors rising constantly from initial of approximately 7 to 8.5 during first 20 days of operations. From day 24 to 39, pH of reactor 3 were fluctuated between 8 and 9 while pH of reactor 1 and 2 continue to rise around 10 and 9.5 respectively. From day 40 to until end of operational period, pH of 3 reactors remained nearly constant around 9.48, 9.45 and 8.43 respectively. The pH of feed water was ranged from 5.5-7.5.

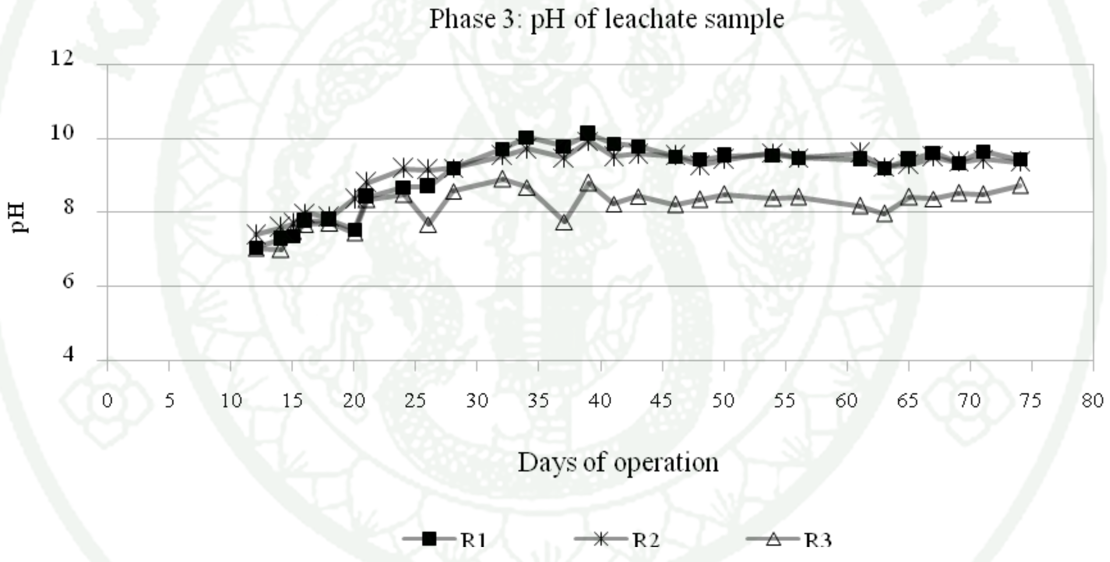


Figure 21 Phase 3: pH of leachate sample

4.2 Gas chromatography result

Result from gas chromatography analysis in Table 7 revealed that denitrification reaction had occurred during the course of reactor operation and this was the explanation for increased of overall pH level of all 3 reactors. The amount of pH increased directly correlate with increasing amount of nitrogen gas generated.

Nitrogen production was influenced by several factors such as initial pH of waste which fall in optimum range for denitrification, nitrate presence in waste body which bacteria use as oxygen source and also significant amount of trace heavy metal

(WPC, 2010) presence as well. Notice that no carbon dioxide was detected indicated possibility that limitation of carbon source is bottleneck of biological degradation process during reactor operation period.

Table 7 Phase 3: Gas chromatography result

Gas composition	Reactor 1	Reactor 2	Reactor 3
CH_4	5.55%, 542 ml	10.41%, 670 ml	16.82%, 897 ml
O_2	1.79%, 175 ml	1.80%, 116 ml	1.79%, 95 ml
N_2	92.65%, 9038 ml	87.79%, 5649 ml	81.40%, 4343 ml
CO_2	N/A	N/A	N/A

4.3 Gas produced during reactor operation

Figure 22 show cumulative gas production of 3 reactors. Gas production of reactor 1 was significantly higher than reactor 2 and 3. Total gas produced were 9775 ml, 6435 ml and 5335 ml for reactor 1,2 and 3 respectively. Gas production rates from reactor 1 were highest while reactor 2 and 3 gave similar amount of gas produced. However this might caused by the error of sampling location and method.

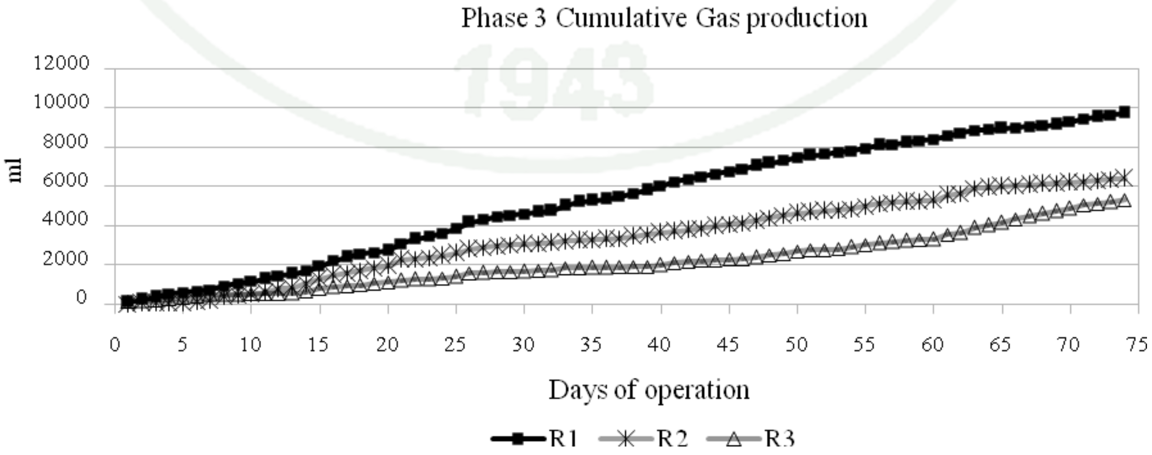


Figure 22 Phase 3: Cumulative gas production

4.4 COD, TDS and VFA leached from reactor

Figure 23 shows cumulative leached of carbon with leachate samples which was computed from leachate chemical oxygen demand (COD) data which were monitored throughout reactors operation. Carbon content leached from reactor 1,2 and 3 were 12.88g, 13.38g and 13.02g respectively. It was found that average chemical oxygen demands (COD) from all 3 reactors were about the same at 12,385 mg/l (range between 10,400 mg/l to 16,000 mg/l) and remained almost constant throughout 74 days operation. Therefore carbon content leached was shown as linear trend. This suggest that there are still more food source available in waste matrix waiting to be hydrolyzed and utilize for biological degradation process.

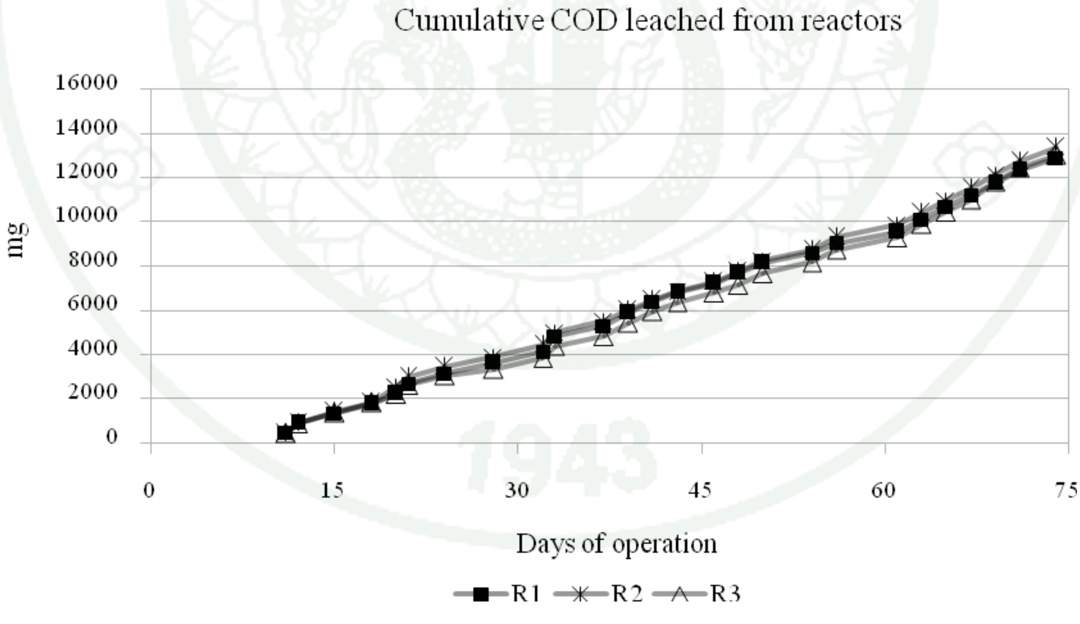


Figure 23 Phase 3: Cumulative COD leached from reactors

Figure 24 shows cumulative leached of total dissolve solid with leachate sample which was computed from total dissolve solid result monitored through out reactors operational period. Total TDS leached from reactor 1, 2 and 3 were 19.23g, 16.78g and 17.67g respectively. Average TDS level for reactor 1 was 19,064 mg/l (range between 15,000 mg/l – 25,000 mg/l). Average TDS level for reactor 2 was lowest among 3 reactors at 16,608 mg/l (range between 12,000 mg/l – 21,000 mg/l). Reactor 3 average TDS level was 17,497 mg/l (range between 13,000 mg/l – 23,000 mg/l). According to figure 27, TDS leached with leachate samples fitted linear trend.

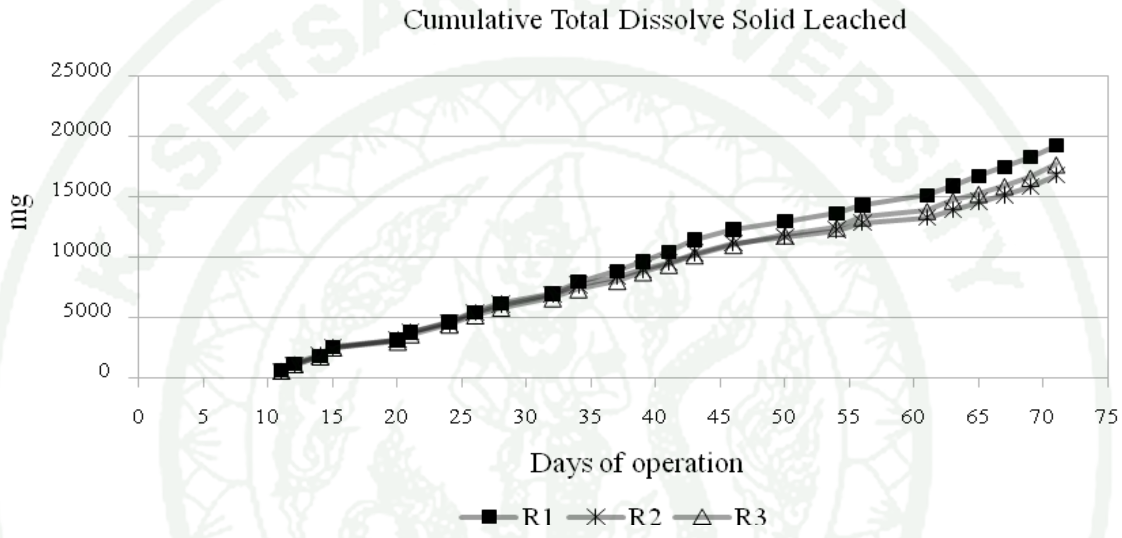


Figure 24 Phase 3: Cumulative TDS leached from reactors

Figure 25 shows cumulative leached of volatile fatty acid with leachate sample which was computed using data from volatile fatty acid level throughout reactor operational period. Volatile fatty acid leached from reactor 1,2 and 3 were 6.88g, 6.32g and 6.83g respectively. It was found that the average concentration of volatile fatty acid in 3 reactors were above 6,000 mg/l (6,114 mg/l for reactor 2 and 6,705 mg/l for reactor 1 and 3). Compared to phase 2 experiments, yield of both volatile fatty acid and gas were much higher which suggested the relationship between gas output and volatile fatty acid in the system. Additionally initial pH condition and rapid rainwater addition of phase 3 experiment encouraged higher reaction rate of microbial activity occurred inside landfill reactors.

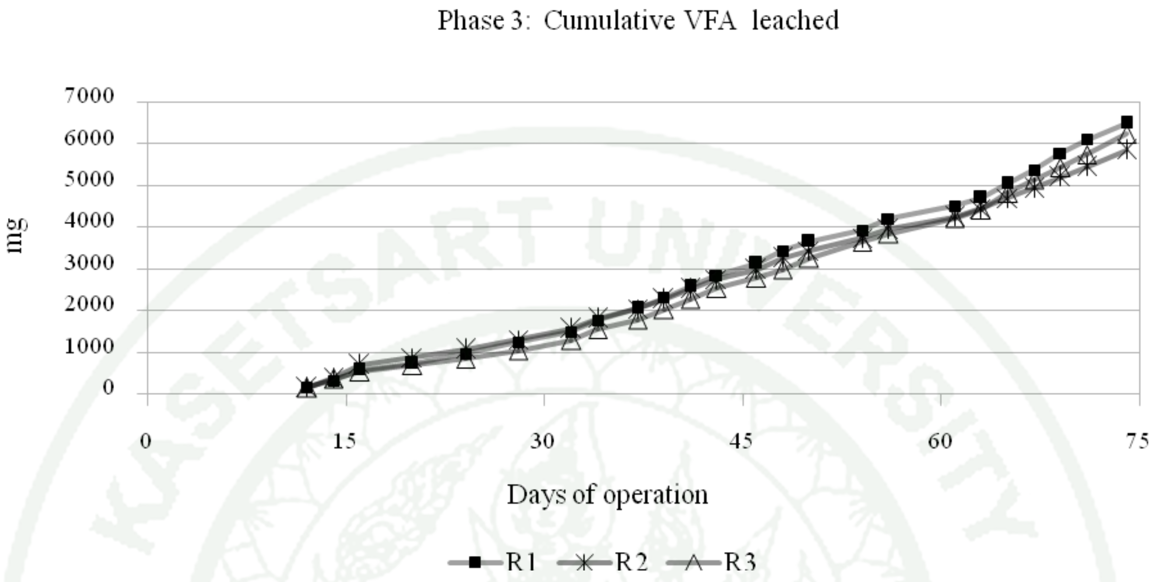


Figure 25 Phase 3: Cumulative VFA leached from reactors

Table 7 show that the initial total organic carbon of 0.3661 kg, 0.4582 kg and 0.5925 kg found from the stabilized waste were reduced to 0.3253 kg, 0.4015 kg and 0.4569 kg from the reactor 1,2 and 3, respectively. Total organic carbon had been reduced by 0.0408 kg, 0.0567 kg and 0.1356 kg respectively.

Table 8 Phase 3: Waste Characteristics after reactor operation

	Reactor 1	Reactor 2	Reactor 3
Total Solid	97.24%	97.71%	97.78%
Fixed Solid	99.69%	99.67%	99.74%
Volatile Solid	0.31%	0.33%	0.26%
Moisture Content	2.76%	2.29%	2.22%
Total Carbon	2.72%	3.24%	3.69%
Total Inorganic Carbon	0.54%	0.55%	0.62%
Total Organic Carbon	2.18%	2.69%	3.07%
Total Organic Carbon in Reactor	0.3253 kg	0.4015 kg	0.4569 kg
Change in Total Organic Carbon	- 0.0408 kg	-0.0567kg	-0.1356 kg

Data from phase 3 can be use in following calculation;

Methane Gas density (1.013 bar and 15 °C (59 °F)) : 0.68 kg/m^3

Nitrogen (N_2) Gas density (1.013 bar and 15 °C (59 °F)) : 1.185 kg/m^3

Reactor 1:

Initial TOC = 0.3661 kg (dry initial TOC 2.46 % x 14.9 Liter)

End TOC = 0.3253 kg (dry end TOC 2.18 % x 14.9 Liter)

Change in TOC = 0.0408 kg

Leachate COD = 0.012880 kg (figure 25)

Leachate VFA = 0.00687953 kg (figure 27)

Leachate TDS = 0.0192309 kg (figure 26)

Methane : 0.00054165 m^3 (table 6) * 0.68 kg/m^3 = 0.000368322 kg

Nitrogen : 0.00903829 m^3 (table 6)* 1.185 kg/m^3 = 0.01071037365 kg

Output = COD + VFA + TDS + Methane + Nitrogen = 0.050069 kg

Reactor 2:

Initial TOC = 0.4582 kg (dry initial TOC 3.08 % x 14.9 Liter)

End TOC = 0.4015 kg (dry end TOC 2.69 % x 14.9 Liter)

Change in TOC = 0.0567 kg

Leachate COD = 0.013376 kg (figure 25)

Leachate VFA = 0.006320.78 kg (figure 27)

Leachate TDS = 0.0167678 kg (figure 26)

Methane : 0.00066987 m^3 (table 6)* 0.68 kg/m^3 = 0.0004555116 kg

Nitrogen : 0.00562926 m^3 (table 6)* 1.185 kg/m^3 = 0.006676731 kg

Output = COD + VFA + TDS + Methane + Nitrogen = 0.0435968226 kg

Remain in reactor = 0.0131 kg

Reactor 3:

Initial TOC = 0.5925 kg (dry initial TOC 3.98 % x 14.9 Liter)

End TOC = 0.4569 kg (dry initial TOC 3.07 % x 14.9 Liter)

Change in TOC = 0.1356 kg

Leachate COD = 0.013024 kg (figure 25)

Leachate VFA = 0.00682875 kg (figure 27)

Leachate TDS = 0.01767055 kg (figure 26)

Methane : 0.00089716 m^3 (table 6)* 0.68 kg/m^3 = 0.0006100688 kg

Nitrogen : 0.00434258 m^3 (table 6)* 1.185 kg/m^3 = 0.0051459573 kg

Output = COD + VFA + TDS + Methane + Nitrogen = 0.0432733261 kg

Remain in reactor = 0.0923266739 kg

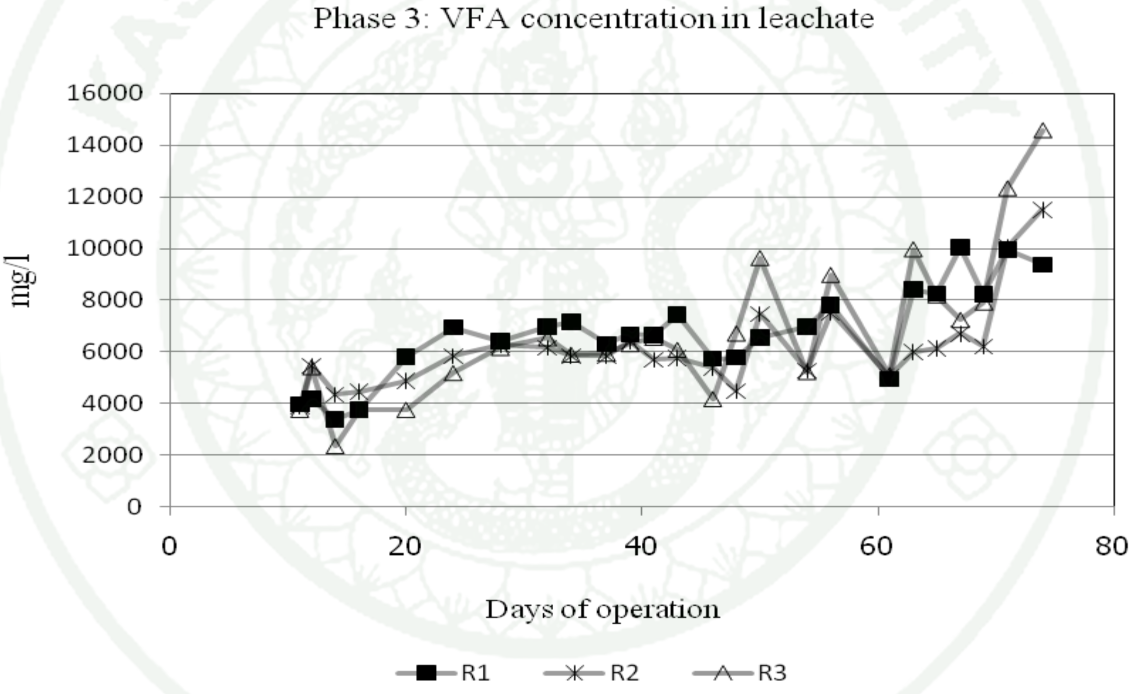


Figure 26 VFA concentration in phase 3 experiment

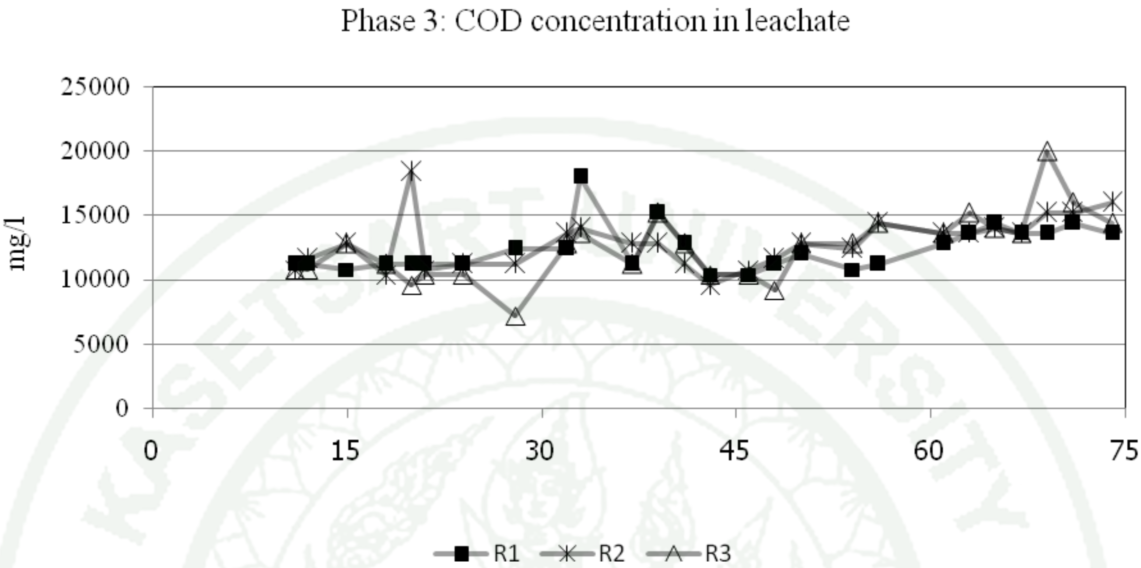


Figure 27 COD concentration in phase 3 experiment

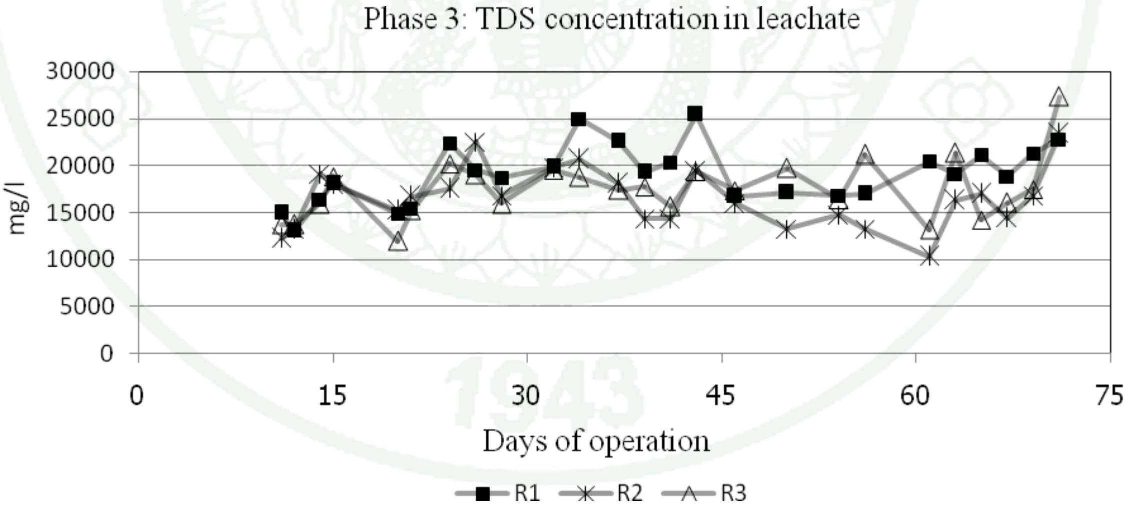


Figure 28 TDS concentration in phase 3 experiment

Figure 26, 27 and 28 show summary of phase 3 leachate analysis which are used to calculate VFA/COD ratio and mass balance in which can be used to describe detail of biological reaction inside reactor

Discussion

1. Phase 1: Leaching Test

Phase 1 leaching test result revealed relationship of decreasing pH and metal leaching. Result show decreased pH of extract fluid cause by increased amount of acetic acid in the system affect on increased concentration of heavy metals. Acetic acid is major by product of biological degradation process in landfill operation. Thus agree to (Nonthawat, 2008) finding which reported relationship of increased total organic carbon (TOC) contamination in stabilized sludge and increased heavy metal concentration in leachate.

Explanation for deviation of Ni and Cr result which had maximum heavy metal concentration at pH 7 instead of 6 is that different heavy metal have different affinity for different type of organic acid. During acidogenesis/acitogenesis phase humic substance in solid phase were decreased and fatty acid were generated from acidogen, result in increase ratio of humic acid/fatty acid during 0.5 to 1.5 years of landfill age. Humic acid has stronger binding capacity than fatty acid, therefore it is harder to leach heavy metal which was bind to humic substance in solid phase. (Xian Qu *et al.,* 2007).

2. Phase 2: Simulated Landfill Reactor Operation

Even though pH remain almost constant from initial to end of operation, there were production of volatile fatty acid and gas in which indicating biological activities within reactors. During reactor operation maximum amount of volatile fatty acid produced was 7.5 g/L, which was approximately one third compare to 20 g/L of municipal solid waste degradation prior to methanogenic stage (Liliana *et al.,* 1997). This show that stabilized hazardous waste had reached acid producing phase despite only 5.17 % of total organic carbon contamination in system. However, in secured landfill case, lesser amount of volatile fatty acid were generated due to much lower food source for acidogenic bacteria therefore volatile fatty acid contributed less degree of effect to both pH and metal leaching compared to municipal solid waste landfill.

Leachate analysis from simulated landfill reactors indicated that there were constant leaching of heavy metal during operational period. Result of Cr and Cd were agree with (Xian Qu *et al.,* 2007) results which also indicated high heavy metal complex leaching out during initial stage of municipal solid waste landfill operation (hydrolysis and acid production phase). Their work indicated large portion of heavy metal is bound to organic substance. Total amount of Cr and Cd leached from 3 experiment replication lies in 95% confidence interval of each other. Despite reactor 3 condition which has lowest initial pH of 10.5 and least amount of volatile fatty acid and gas produced. This phenomenon indicated that heavy metal retaining capability of waste was also significantly depend on initial pH of stabilized waste body (Bozkurt *et al.,* 1999).

Leaching of heavy metal in phase 2 experiment were confirmed. Results were above Thailand's pollution control department underground water standard which require cadmium (Cd) and hexavalent chromium (Cr) concentration to be lesser than 0.003 mg/L and 0.05 mg/L respectively.

3. Phase 3: Simulated landfill reactor Operation

3.1 VFA/COD ratio

Chemical oxygen demand measure the capacity of water to consume oxygen during decomposition of organic matter and oxidation of inorganic chemical such as nitrite or ammonia. During acidogenesis/acitogenesis phase, volatile fatty acid was rapidly generated and use up COD in the hydrolyzed form result in steady increasing trend of VFA/COD ratio in 3 reactors. During methanogenic phase VFA were used and ratio lowered. Low VFA/COD ratio suggested that there were low amount of readily degradable carbon source for acidogenic bacteria to utilized. In long term operation, VFA/COD ratio which did not decrease overtime indicated inhabition of acetogenesis due to accumulation of undissociated VFA. (Borzacconi *et al.*, 1997) .

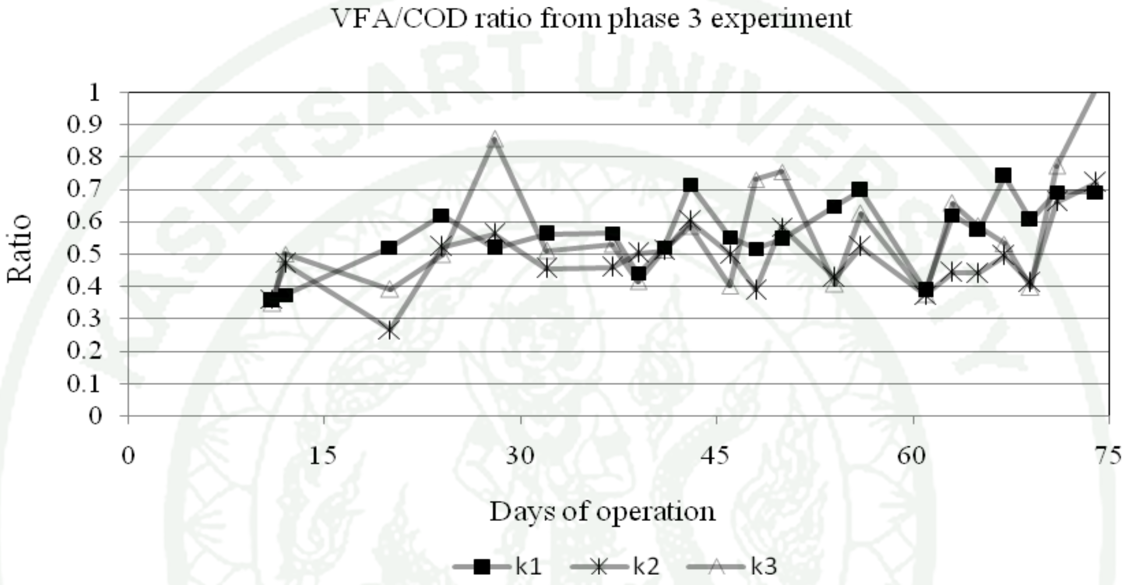


Figure 29 VFA/COD ratio for phase 3 simulated landfill reactors experiment

At the beginning of reactors operation ratio to minimum on day 20 at 0.27 and 0.39 for reactor 2 and 3 respectively. This suggest that in the beginning, acidogenesis phase has been established. VFA/COD ratio of phase 3 reactor 1, 2 and 3 were range between 0.4 – 0.6 for 3 reactors from day 24 to day 67. From day 71 toward the end of experiment, ratio went up to maximum value at 0.74, 0.72 and 1.0 for reactor 1, 2 and 3 respectively. High VFA/COD ratio, with values ranging from about 0.8 to 1.0 indicating that hydrolysis was the rate-limiting step (Maharaj and Elefsiniotis, 2000) of volatile fatty acid production.

As the reactors operate for longer the system require more amount of water to hydrolysis carbon source from hazardous waste stabilized matrix. In short term, amount of readily degradable and initial pH predominantly controlled leaching. However, long term leaching were controlled by amount of hydrolysis reaction.

3.2 Denitrification, hydrolysis of organic compound and increased pH

Result form gas chromatography analysis revealed that gas produced from reactor 1, 2 and 3 contain 92.65 %, 87.79 % and 81.40 % respectively. It is possible that denitrifying bacteria use nitrate in stabilized hazardous waste body as primary oxygen source and carbon source in waste body as its food resulting nitrate reduced to nitrogen gas. Throughout phase 3 experiment, pH level ranged from 7.3-9.5 for reactor 1, 2 and 7.0-8.5 for reactor 3. This is close to optimum pH of denitrification reaction of 7.0-8.5. Also acetic acid and methanol are carbon source that yield highest growth rate for denitrification bacteria (Water Planet Company). Therefore reduction of carbon source within system didn't depend entirely on either acidogenesis and methanogenic reaction but also denitrification as well. However, nitrate analysis of waste material is required as proof to this phenomenon.

According to figure 23 from result section, initial pH were 7.07, 7.41 and 7.01 for reactor 1,2 and 3 respectively. According to literature review, denitrification reaction is an alkalinity producing process. Therefore this explained increased of 3 reactors pH level from day 18 onward. From day 41 onward, pH level stabilized around 9.5 for reactor 1,2 and 8.45 for reactor 3 this might occurred due to buffer capacity of stabilized hazardous waste.

Hydrolysis of organic compound from stabilized waste body might also cause increase pH of leachate. Since the waste matrix was stabilized with lime, addition of water into system hydrolyzed it result in increased pH leachate even though VFA were produced by biological degradation.

Mass Balance

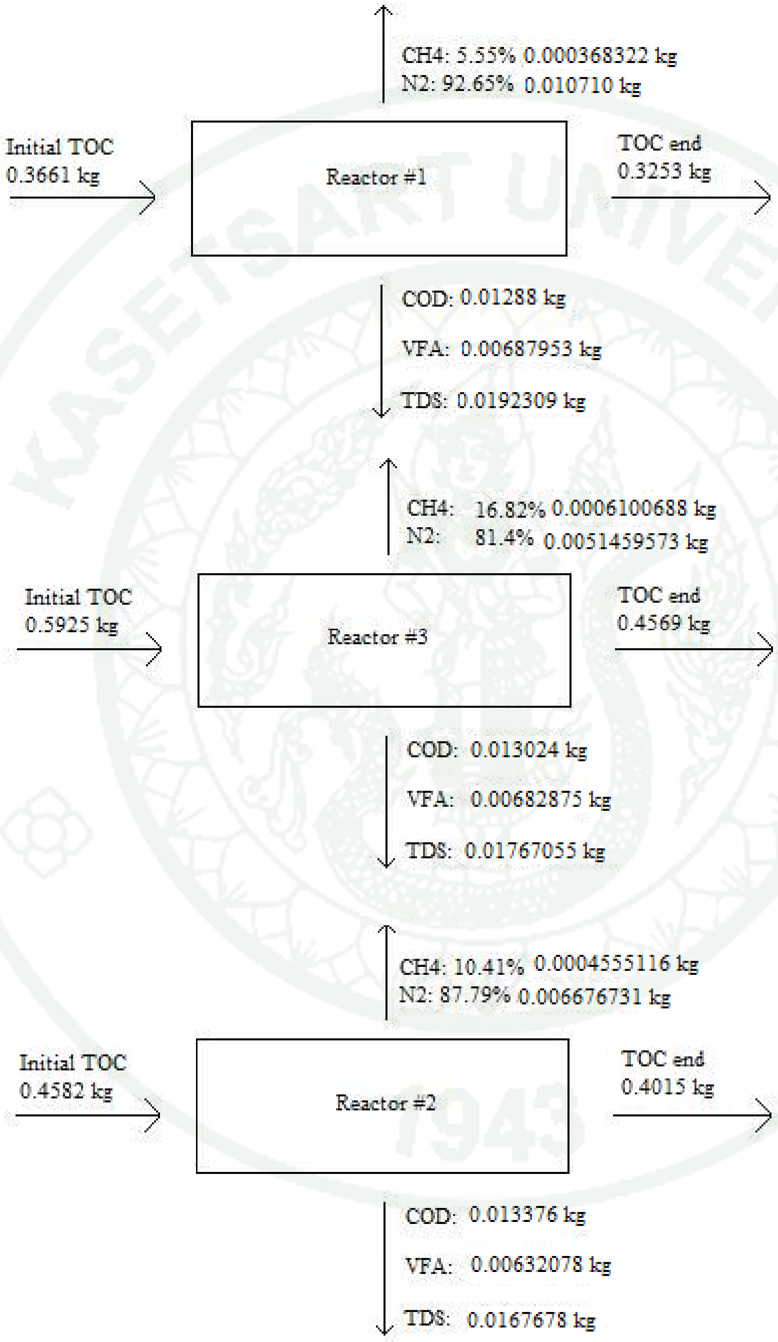


Figure 31 Mass Balance of 3 simulated landfill reactors

Mass balance analysis revealed cause for reduction of total organic carbon from the system. Total organic carbon in waste body were reduced by several process such as;

1. Used as carbon source by acidogenesis bacteria to generate VFA
2. Used as carbon source by denitrification bacteria to generate nitrogen gas
3. Used as carbon source by methanogenic bacteria to generate methane gas
4. Leached out in total dissolve solid (TDS) and suspended solid (SS) form
5. Form organic complex (Chelation) and leached out along with HMS

Mass balance analysis is the main objective of phase 3 reactors operation. Amount of mass output from reactor can be compute by;

Output = Accumulate COD leached + Accumulate VFA leached + Accumulate TDS leached + Amount of Nitrogen generated + Amount Methane generated

Theoretically, output must be equal to difference of initial and end total organic carbon amount. Imbalance can be explained by that organic carbon were either still in process of hydrolysis and conversion to end product, could be converted to cell mass itself or in form of volatile fatty acid which still remained to be process by acidogenesis bacteria, methanogenic bacteria and denitrifying bacteria inside reactor.

CONCLUSION AND RECOMMENDATION

Conclusion

On phase 1 experiment, reducing pH caused by effect of acetic acid had increased heavy metal concentration in leachate which confirm hypothesis of heavy metal leaching increased with increasing acetic acid. TCLP result in phase 1 had given comparable trend with WET method (Nonthawat, 2008). Earlier works revealed that volatile fatty acid (acetiate, propionate and butyrate) have high affinity for heavy metals especially in bioreactor condition which moisture content exceed 60% (Xian Qu *et al.,* 2008).

Phase 2 experiment results confirm that although the hazardous waste was stabilized under an extreme condition (pH = 10-12), the micro-organisms were still able to transform the total organic carbon under anoxic condition. This was proven by an increase of volatile fatty acid and gas production from the leachate during the lab-scale landfill reactor operation. Moreover, VFA production does not caused pH reduction in the leachate due to buffer capacity of the waste. However, heavy metal concentrations is present the leachate. Accordance to Thailand's underground water regulation, leachate from hazardous secured landfill operation require treatment to remove heavy metal prior to discharge.

VFA and COD ratio during phase 3 experiment indicated that as the reactors operate for longer, system require more amount of water to hydrolyze carbon source from hazardous waste stabilized matrix. During initial landfill stage, low VFA/COD ratio suggested that there were low amount of readily degradable carbon source for acidogenic bacteria to utilized. When rainwater seep into waste column after 10 days then ratio increase constantly which indicated that amount of readily degradable and initial pH predominantly controlled leaching. However, VFA/COD ratio rise to indicated that longer term leaching were controlled by amount of hydrolysis reaction (Maharaj and Elefsiniotis, 2000)

Mass Balance draw conclusion that total organic carbon in stabilized industrial waste sludge has been converted to end product by following type of microorganism;

1. Acidogenesis bacteria
2. Methanogenic bacteria
3. Denitrifying bacteria

These reaction create following product;

1. Volatile Fatty Acid (VFA)
2. Methane Gas (CH_4)
3. Nitrogen Gas (N_2)

The water hydrolysis total organic carbon to be converted to volatile fatty acid (VFA) by acidogenesis bacteria. While in anoxic condition, Methanogenic and denitrifying then both utilize volatile fatty acid as carbon source to generate methane gas (CH_4) and nitrogen gas (N_2). Even though system content less than 5% of organic carbon source, biological activities is still detectable.

Recommendation

Recommendations are as following;

1. The result indicate that rain water seepage into stabilized waste body is the long term cause for metal leaching from secured landfill operation. To minimize biological reaction and heavy metal leaching, leachate collection system must keep waste body to maintained at lowest moisture content possible. This can be further investigate to determine end point of heavy metal leaching once organic carbon source has been used up

2. Stabilized waste also came with clay/soil like texture; therefore stabilization process by port land cement might be better choice to reduce solubility of hazardous waste body. Study to minimize solubility of hazardous waste due to different type and proportion of solidification agents can be further investigate.

3. Relieve venting is require since biological reaction created enough gas to increase pressure inside laboratory scale reactor.

4. Initial pH level of stabilized hazardous waste entering landfill is also important factor for solubility of heavy metal and intensity of biological activity inside reactor. At initial pH 7.5-8.5, amount of gas generated were 3 times compare to waste with initial pH of 11-12.

5. Amount of nitrate in stabilized hazardous waste could be investigate since nitrate is alkaline producing reaction, Therefore addition of nitrate waste in the mix might help to maintain pH of stabilized waste body.

LITERATURE CITED

American Public Health Association. 21st Edition, 2005. Standard Methods For The Examination of Water and Wastewater, **Method 5310 B; Total Organic Carbon (TOC), High-Temperature Combustion Method**.

American Society for Microbiology Applied Environmental Microbiology. 1975. **Environmental Biotechnology: concepts and application: Chapter 14.**

Ahmed M. Emam, Brian D. Barkdoll, Kenneth L., McManis and Marty E. Tittlebaum. 2004. **Issues and research needs for the wet-cell Landfill approach**

A. Suna Erses, Turgut T. and Onay Bo gaziçi. 2005. **In situ heavy metal attenuation in landfills under methanogenic conditions.** University Institute of Environmental Sciences, Istanbul, Turkey.

Bozkurt S., Moreno L. and Neretmieks I., 1999. **Long-term process in waste deposit Sci. Total Environment.** Volume 250 pp. 101-121**.**

Clair N. Sawyer, Perry L. Mccarty and Gene F. Parkin. 2003. **Chemistry for environmental engineering and science,** Fifth Edition Chapter 12 and 13

Department of Toxic Substances Control California Environmental Protection Agency **Comparison of TCLP and WET test method**

Environmental Protection Agency [EPA], Test method 1311, 1992 **Toxicity Characteristic Leaching Procedure**

Environmental Protection Agency. [USEPA]. 1989. **Requirement for Hazardous Waste Landfill Design, Construction and Closure**

F.G Pohland, in: J.F. Malina, F.G. Poh land (Eds.), 1992,**Design of Anaerobic Processes for the treatment of industrial and municipal waste**, Vol 7, Technomic Publishing Co., Lancaster, PA, pp.1-41

General Environmental Conservation Public Co., Ltd., 2005. **Facility and Treatment.** Available on the website: http://www.genco.co.th/

Hooper K, Iskander M, Silva G, Hussein F, Hsu J and deGuzman. 2004. **Hydrolytic and methanogenic inhibition,** ISSN 1618-2650.

Iram San and Turgut T. Onay. 2001. **Impact of various leachate recirculation regimes on municipal solid waste degradation.** Springer Link/ Heidelberg.

I. Maharaj and P. Elefsiniotis. 2000. **The role of HRT and low temperature on the acid-phase anaerobic digestion of municipal and industrial wastewaters.** ScienceDirect Bioresource Technology.

Liliana Borzacconi, Ivan Lopez and Carlos Anido. 1997. **Hydrolysis constant and VFA inhibition in acidogeneic phase of msw anaerobic degradation.** IWA publishing Water Science and Technology.

Imperial College London **Waste management course.** n.p.

Martin, A.D. 2007. **Understanding Anaerobic Digestion, Presentation to the Environmental Services Association**. esauk.org.

Nontawat nuttapun. 2008. **Total Organic Compound Contamination study from secure landfill leachate during operation**. Kasetsart university.

Obuli P., Karthikeyan and Kurian Joseph. 2007. **Bioreactor Landfill for Sustainable Solid Waste Management.** Centre of Environmental Studies, Anna University.

Pollution Control Department. 2010. **Thailand community originated Hazardous waste management and law.** Avaliable Source: Hazwaste@pcd.go.th

Qin Wang. 2004. **Aspects of Pretreated Hospital Waste degradation in Landfill.** Gerhard-Mercator-Universitaet Duisburgb

R. Taylor and A. Allen. 2006. **Waste disposal and landfill information** World Health Organization. Avaliable source: www.who.int/water_sanitation_health/resourcesquality/en/groundwater12.pdf

Schink, B. 1997. **Energetics of syntrophic cooperation in methanogenic degradation, Microbiology and MolecularBiology.** American Society for Microbiology

Shou-liang Huo, Bei-dou Xi, Hai-chan Yu, Shi-lei Fan, Su Jing and Hong-liang Liu. 2008. **A laboratory simulation of in situ leachate treatment in semi-aerobic bioreactor landfill** Water Research Commision, Pretoria.

Prof. Dr. Sombat Teekasap. **Intergrated waste and energy situation in Thailand Lecture.** n.p.

Pin-Jing He , Li-Ming Shao, Xian Qu, Guo-Jian Li, Duu-Jong Lee. State Key. 2006. **Effects of feed solutions on refuse hydrolysis and landfill leachate characteristics.** Laboratory of Pollution Control and Reclamation, Department of Environmental Engineering, Tongji University China, Department of Chemical Engineering, National Taiwan University

United Nation Environmental Programme [UNEP]. 1985. **Definition of Hazardous Waste**

Vasily A. Vavilin, Susanne Jonsson, Jorgen Ejlertsson and Bo H. Svensson. 2006. **Modelling MSW decomposition under landfill conditions considering hydrolytic and methanogenic inhibition.** Environmental Science Technology 32:3825

The Water Planet Company. **Nitrification and Denitrification article**

Xian Qu, Pin-Jing He, Li-Ming Shao, Duu Jong Lee. 2008. **Heavy metals mobility in full-scale bioreactor landfill Initial stage.**

APPENDICES

Appendix A
Stabilized Hazardous Sludge Analysis TS, FS, VS, Moisture and TOC

Appendix Table A1 Initial Sludge Analysis TS, FS, VS and Moisture parameter prior to Phase 1 & Phase 2

	Initial weight (g)	Weight after 105C (g)	Total solid (%)	Weight after 550C (g)	Fixed solid (%)	Volatile solid (%)	Moisture (%)
R,1,2,3 initial	47.6694	46.6554	97.8728	46.4418	99.5422	0.4578	2.1272
	48.3294	47.3252	97.9222	47.1118	99.5491	0.4509	2.0778
	42.4540	41.4449	97.6231	41.1989	99.4064	0.5936	2.3769
	49.3709	48.3933	98.0199	48.1428	99.4824	0.5176	1.9801
	56.4425	55.4410	98.2256	55.2165	99.5951	0.4049	1.7744
	41.9162	40.9318	97.6515	40.6764	99.3760	0.6240	2.3485
	47.0905	46.1225	97.9444	45.8862	99.4877	0.5123	2.0556
	38.6713	37.6730	97.4185	37.4935	99.5235	0.4765	2.5815

Note** Phase 2 reactor, each loaded with 17.1 kg of stabilized hazardous waste
Avg. total solid for sample (%) = 97.8348 % or 16.73kg in reactor
Avg. moisture for sample (%) = 2.1652 %
Avg. fixed solid for sample (%)= 99.4953 % or 16.65 kg in reactor
Avg. volatile solid for sample (%) = 0.5047 % or 0.0844 kg in reactor

Appendix Table A2 Phase 2: Raw Data of Sludge Analysis TS, FS, VS and Moisture parameter after Phase 2

	Initial weight (g)	Weight after 105C (g)	Total solid (%)	Weight after 550C (g)	Fixed solid (%)	Volatile solid (%)	Moisture (%)
R1	56.4269	55.7499	98.8002	55.6602	99.8391	0.1609	1.1998
	56.7911	55.8083	98.2694	55.6556	99.7264	0.2736	1.7306
	47.7076	46.9047	98.3170	46.7814	99.7371	0.2629	1.6830
R2	47.6477	46.5699	97.7380	46.4225	99.6835	0.3165	2.2620
	48.6396	47.5133	97.6844	47.3441	99.6439	0.3561	2.3156
	41.9462	40.8259	97.3292	40.6508	99.5711	0.4289	2.6708
R3	47.0814	45.8834	97.4555	45.7222	99.6487	0.3513	2.5445
	75.2149	74.0092	98.3970	73.8216	99.7465	0.2535	1.6030
	56.6451	55.4703	97.9261	55.3066	99.7048	0.2952	2.0739

Appendix Table A3 Phase 2: Summary of Sludge Analysis TS, FS, VS and Moisture parameter after Phase 2

	Avg. total solid (%)	Total solid in reactor (kg)	Avg. fixed solid (%)	Fixed solid in reactor (kg)	Avg. volatile solid (%)	Volatile solid in reactor (kg)	Avg. moisture (%)
R1	98.4622	16.8370	99.7675	16.7979	0.2325	0.0393	1.5378
R2	97.5839	16.6868	98.2694	16.6256	0.3672	0.0614	2.4161
R3	97.9262	16.7454	99.7000	16.6947	0.3000	0.0504	2.0738

Note** Phase 2 reactors, each loaded with 17.1 kg of stabilized hazardous waste

Appendix Table A4 Phase 2: Initial TOC analysis

	TC Sample weight (mg)	Total carbon detected (µg)	Total carbon (%)	IC Sample weight (mg)	Inorganic carbon detected (µg)	Inorganic carbon (%)	Total Organic Carbon (µg)
R,1,2,3 initial	102.9	6098	5.93%	99.8	978	0.98%	5120
	112.3	7320	6.52%	100.3	754	0.75%	6566
	101.1	6194	6.13%	111.1	1104	0.99%	5090
	101.7	6384	6.28%	109.8	1098	1.00%	5286

Note** Avg. total carbon (%) = 6.21%
Avg. inorganic carbon (%) = 0.93%
Avg. total organic carbon (%) = 5.28%
Actual total organic carbon considering moisture content(%) = 5.17%
Total organic carbon in reactor (kg) = 0.8834 kg

Appendix Table A5 Phase 2: Raw data of TOC analysis after 90 days reactors operation

	TC Sample weight (mg)	Total carbon detected (µg)	Total carbon (%)	IC Sample weight (mg)	Inorganic carbon detected (µg)	Inorganic carbon (%)	Total Organic Carbon (µg)
R1	115.8	5326	4.60%	102	1198	1.17%	4064
	100.8	4952	4.91%	108.8	1173	1.08%	3721
	111.1	5179	4.66%	101.4	923.9	0.91%	4190
R2	100.8	5010	4.97%	102.5	926.1	0.90%	3985
	109.9	4840	4.40%	108	863.8	0.80%	3880
	117.8	5513	4.68%	101.5	1130	1.11%	4277
R3	110.2	5577	5.06%	101.5	935.8	0.92%	4545
	100.1	5071	5.07%	101.1	802.6	0.79%	4179
	113.6	6310	5.55%	106.1	891.9	0.84%	5306

Appendix Table A6 Phase 2: Summary of TOC analysis after 90 days reactors operation

	Avg. total carbon (%)	Avg. inorganic carbon (%)	Avg. TOC (%)	Avg. moisture (%)	Actual TOC consider moisture (%)	TOC in reactor (kg)
R1	4.73%	1.06%	3.67%	1.5378	3.61%	0.6179
R2	4.68%	0.94%	3.75%	2.4161	3.66%	0.6251
R3	5.23%	0.85%	4.37%	2.0738	4.28%	0.7326

Appendix Table A7 Phase 3: Summary of Sludge Analysis TS, FS, VS and Moisture parameter prior to Phase 3

	Avg. total solid (%)	Total solid in reactor (kg)	Avg. fixed solid (%)	Fixed solid in reactor (kg)	Avg. volatile solid (%)	Volatile solid in reactor (kg)	Avg. moisture (%)
R1	98.4622	16.8370	99.7675	16.7979	0.2325	0.0393	2.48%
R2	97.5839	16.6868	98.2694	16.6256	0.3672	0.0614	3.14%
R3	97.9262	16.7454	99.7000	16.6947	0.3000	0.0504	2.68%

Note** Phase 3 reactors, each loaded with 14.9 kg of stabilized hazardous waste

Appendix Table A8 Phase 3: Raw Data of Sludge Analysis TS, FS, VS and Moisture parameter after Phase 3

	Initial weight (g)	Weight after 105C (g)	Total solid (%)	Weight after 550C (g)	Fixed solid (%)	Volatile solid (%)	Moisture (%)
R1	49.4125	48.1346	97.4138	47.9998	99.7200	0.2800	2.5862
	42.4627	41.2163	97.0647	41.0803	99.6700	0.3300	2.9353
R2	48.3305	47.1391	97.5349	46.9612	99.6226	0.3774	2.4651
	58.1326	56.9039	97.8864	56.7479	99.7259	0.2741	2.1136
R3	56.4508	55.2036	97.7906	55.0470	99.7163	0.2837	2.2094
	56.6509	55.3885	97.7716	55.2601	99.7682	0.2318	2.2284

Appendix Table A9 Phase 3: Summary of Sludge Analysis TS, FS, VS and Moisture parameter after Phase 3

	Avg. total solid (%)	Total solid in reactor (kg)	Avg. fixed solid (%)	Fixed solid in reactor (kg)	Avg. volatile solid (%)	Volatile solid in reactor (kg)	Avg. moisture (%)
R1	97.24%	14.49	99.69%	14.44	0.31%	0.044	2.76%
R2	97.71%	14.56	99.67%	14.51	0.33%	0.047	2.29%
R3	97.78%	14.57	99.74%	14.53	0.26%	0.038	2.22%

Note** Phase 3 reactors, each loaded with 14.9 kg of stabilized hazardous waste

Appendix Table A10 Phase 3: Raw data of initial TOC analysis

	TC Sample weight (mg)	Total carbon detected (µg)	Total carbon (%)	IC Sample weight (mg)	Inorganic carbon detected (µg)	Inorganic carbon (%)	Total Organic Carbon (µg)
R1	109	3045	2.79%	104.1	415.6	0.40%	2564
	100.3	2770	2.76%	122.8	525	0.43%	2189
	115.6	3814	3.30%	105.4	493.6	0.47%	3238
R2	131.9	5749	4.36%	127.8	604.3	0.47%	4983
	107.2	3493	3.26%	116.9	406.3	0.35%	2990
	116.2	3757	3.23%	113.4	572.5	0.50%	3084
R3	108.2	5109	4.72%	111.3	594.9	0.53%	4393
	120	4866	4.06%	115.2	694.4	0.60%	4060
	122.5	6242	5.10%	119.5	570.2	0.48%	5520

Appendix Table A11 Phase 3: Summary of phase 3 initial TOC analysis

	Avg. total carbon (%)	Avg. inorganic carbon (%)	Avg. TOC (%)	Avg. moisture (%)	Actual TOC consider moisture (%)	TOC in reactor (kg)
R1	2.95%	0.43%	2.52%	2.48%	2.46%	0.3661
R2	3.62%	0.44%	3.18%	3.14%	3.08%	0.4582
R3	4.62%	0.54%	4.09%	2.68%	3.98%	0.5925

Appendix Table A12 Phase 3: Raw data of TOC analysis after 75 days reactors operation

	TC Sample weight (mg)	Total carbon detected (µg)	Total carbon (%)	IC Sample weight (mg)	Inorganic carbon detected (µg)	Inorganic carbon (%)	Total Organic Carbon (µg)
R1	96.8	2977	3.08%	118.6	605.2	0.51%	2371.8
	114.1	3061	2.68%	94	540	0.57%	2521
	116.7	3029	2.60%	118.6	605.2	0.51%	2423.8
	152.6	4319	2.83%	106.8	648.5	0.61%	3670.5
R2	117.9	3551	3.01%	105.5	564.5	0.54%	2986.5
	129.5	4011	3.10%	133.4	806.8	0.61%	3204.2
	112.1	4325	3.86%	102.5	593.5	0.58%	3731.5
	121.5	4023	3.31%	101.5	535.1	0.53%	3487.9
R3	106.9	3478	3.25%	116.4	748.3	0.64%	2729.7
	127.3	6436	5.06%	110.6	787.3	0.71%	5648.7
	146.4	5019	3.43%	103.9	720.2	0.69%	4298.8
	120.3	4102	3.41%	135.2	674.3	0.50%	3427.7

Appendix Table A13 Phase 3: Summary TOC analysis after 75 days reactors operation

	Avg. total carbon (%)	Avg. inorganic carbon (%)	Avg. TOC (%)	Avg. moisture (%)	Actual TOC consider moisture (%)	TOC in reactor (kg)
R1	2.80%	0.55%	2.25%	2.76%	2.18%	0.3253
R2	3.32%	0.56%	2.76%	2.29%	2.69%	0.4015
R3	3.03%	0.64%	2.39%	2.22%	2.34%	0.3486

Appendix B

Leachate Analysis Heavy metal, pH, VFA, COD, TDS

Appendix Table B1 Phase 1: Heavy metal analysis of extract fluid

	pH	Sample 1 HM concentration (mg/l)	Sample 2 HM concentration (mg/l)
Cr	10	3.732	8.88
	9	5.44	5.74
	8	7.46	8.34
	7	9.9	10.56
	6	8.36	10.06
Ni	10	1.399	1.984
	9	0.869	1.012
	8	1.064	1.284
	7	1.665	2.446
	6	1.703	2.119
Pb	10	0.442	0.502
	9	0.522	0.552
	8	0.600	0.685
	7	0.667	0.648
	6	0.747	0.803
Cd	10	0.017	0.019
	9	0.023	0.025
	8	0.027	0.029
	7	0.030	0.035
	6	0.041	0.042

Appendix Table B2 Phase 1 raw data: Heavy metal analysis of extract fluid by AAS

Element	pH	Sample 1 HM concentration (mg/l)	Sample 2 HM concentration (mg/l)
Pb	10	0.469	0.516
		0.445	0.511
		0.411	0.478
	9	0.493	0.549
		0.531	0.581
		0.541	0.525
	8	0.559	0.672
		0.603	0.693
		0.636	0.690
	7	0.738	0.645
		0.694	0.633
		0.570	0.664
	6	0.762	0.816
		0.755	0.833
		0.724	0.761
Ni	10	1.388	1.980
		1.401	1.994
		1.408	1.979
	9	0.864	1.010
		0.885	1.003
		0.858	1.023
	8	1.075	1.280
		1.070	1.279
		1.048	1.293
	7	1.686	2.449
		1.652	2.458
		1.657	2.432
	6	1.719	2.122
		1.689	2.109
		1.701	2.126

Appendix Table B2 (Continued)

Element	pH	Sample 1 HM concentration (mg/l)	Sample 2 HM concentration (mg/l)
Cr	10	3.732	0.441 x 20
		3.734	0.443 x 20
		3.728	0.450 x 20
	9	0.271 x 20	0.284 x 20
		0.273 x 20	0.289 x 20
		0.272 x 20	0.288 x 20
	8	0.372 x 20	0.414 x 20
		0.369 x 20	0.416 x 20
		0.379 x 20	0.422 x 20
	7	0.491 x 20	0.526 x 20
		0.496 x 20	0.530 x 20
		0.497 x 20	0.529 x 20
	6	0.413 x 20	0.502 x 20
		0.419 x 20	0.501 x 20
		0.422 x 20	0.507 x 20
Cd	10	0.017	0.021
		0.016	0.020
		0.017	0.017
	9	0.023	0.027
		0.026	0.025
		0.020	0.022
	8	0.028	0.031
		0.029	0.029
		0.025	0.028
	7	0.033	0.035
		0.030	0.035
		0.028	0.036
	6	0.039	0.043
		0.039	0.041
		0.044	0.041

Appendix Table B3 Phase 2 raw data: VFA analysis of leachate

Days of operation	R1 VFA conc. (mg/l)	R2 VFA conc. (mg/l)	R3 VFA conc. (mg/l)
0			
1			
2			
3			
4			
5			
6			
7			
8			
9			
10			
11			
12			
13			
14			
15			
16	6975	6015	3435
17			
18			
19			
20			
21			
22			
23			
24			
25			
26			
27			
28	6300	5940	4410
29			
30			
31			
32			
33			
34	6120	5340	2790
35			
36			
37	8910	4830	1950
38			
39			
40			
41	6000	5880	3540
42	6225	5340	4395
43	6990	8520	3100

Appendix Table B3 (Continued)

Days of operation	R1 VFA conc. (mg/l)	R2 VFA conc. (mg/l)	R3 VFA conc. (mg/l)
44			
45	5910	4755	3780
46			
47			
48	8370	6870	4080
49	6480	5130	3870
50			
51			
52			
53	5160	3750	3900
54			
55			
56	6390	5715	4050
57			
58	6630	5610	3900
59	7520	4860	3930
60			
61			
62			
63	7590	4710	3810
64	6090	5970	4800
65	5850	4680	3645
66	5970	5010	4050
67			
68			
69	5475	4950	3945
70	7080	4485	4050
71			
72	6210	4860	4320
73		4950	4230
74			
75			
76	6225	6645	4155
77	8880	6330	5235
78			
79	7680	6270	5070
80			
81	6510	5820	4350
82			
83	5385	6915	3900
84	5655	5295	4275

Appendix Table B4 Phase 2 raw data: pH analysis of leachate

Days of operation	R1 pH	R2 pH	R3 pH
0			
1			
2			
3			
4			
5			
6			
7			
8			
9			
10			
11			
12			
13			
14			
15			
16	12.32	11.3	9.36
17			
18			
19			
20			
21			
22			
23			
24			
25			
26			
27			
28	12.27	12.26	10.3
29			
30			
31			
32			
33			
34	12.21	12.19	10.6
35			
36			
37	12.25	12.33	10.69
38			
39			
40			
41	12.05	12.13	10.66
42	12.35	12.17	10.64
43	12.35	12.21	10.75

Appendix Table B4 (Continued)

Days of operation	R1 pH	R2 pH	R3 pH
44			
45	12.43	12.24	10.72
46			
47			
48	12.33	12.35	10.62
49	12.4	12.24	10.64
50			
51			
52			
53	12.38	12.18	10.38
54			
55			
56	12.26	12	10.38
57			
58	12.24	12	10.38
59	12.43	12.16	10.44
60			
61			
62			
63	12.56	12.32	10.45
64	12.55	12.34	10.55
65	12.59	12.34	10.54
66	12.54	12.28	10.39
67			
68			
69	12.5	12.32	10.41
70	12.5	12.28	10.47
71			
72	12.35	12.16	10.29
73	12.27	12.26	10.49
74			
75			
76	12.04	11.86	10.13
77	11.94	11.6	10.03
78			
79	12.2	12.14	10.08
80			
81	12.32	12.09	10.17
82			
83	12.35	12.25	10.27
84	12.32	12.13	10.33

Appendix Table B5 Phase 2 raw data: Cd analysis of leachate by AAS

Element	Days of operation	R1 HM concentration (mg/l)	R2 HM concentration (mg/l)	R3 HM concentration (mg/l)
Cd	17	0.028	0.028	0.028
		0.033	0.024	0.031
		0.030	0.025	0.031
	29	0.031	0.038	0.042
		0.030	0.043	0.046
		0.036	0.040	0.044
	44	0.037	0.036	0.049
		0.036	0.040	0.046
		0.029	0.046	0.039
	55	0.038	0.047	0.047
		0.038	0.043	0.045
		0.040	0.040	0.047
	73	0.032	0.051	0.053
		0.037	0.045	0.057
		0.036	0.057	0.055
	85	0.063	0.068	0.060
		0.062	0.064	0.060
		0.065	0.067	0.064

Appendix Table B6 Phase 2 raw data: Cr analysis of leachate by AAS

Element	Days of operation	R1 HM concentration (mg/l)	R2 HM concentration (mg/l)	R3 HM concentration (mg/l)
Cr	17	0.163	0.238	0.360
		0.165	0.236	0.368
		0.172	0.236	0.368
	29	0.174	0.219	0.215
		0.168	0.244	0.222
		0.173	0.244	0.217
	44	1.543	1.094	0.431
		1.518	1.104	0.424
		1.523	1.111	0.435
	55	0.305	0.344	0.289
		0.314	0.358	0.275
		0.332	0.362	0.293
	73	0.288	0.126	0.119
		0.293	0.126	0.117
		0.309	0.138	0.119
	85	0.864	0.750	0.247
		0.861	0.750	0.253
		0.859	0.751	0.252

Appendix Table B7 Phase 3 raw data: pH analysis of leachate

Days of operation	R1 pH	R2 pH	R3 pH	Feed water pH
0				
1				
2				
3				
4				
5				
6				
7				
8				
9				
10				
11	7.07	7.41	7.05	6
12	7.3	7.61	7.01	5.9
13				
14	7.38	7.71	7.51	6.54
15	7.78	8.01	7.7	5.7
16	7.82	7.88	7.73	5.73
17				
18	7.55	8.38	7.47	6.32
19				
20	8.43	8.82	8.36	5.91
21	8.69	9.2	8.5	5.62
22				
23				
24	8.71	9.16	7.7	5.53
25				
26	9.21	9.22	8.59	5.85
27				
28	9.73	9.54	8.92	5.6
29				
30				
31				
32	10.04	9.73	8.7	6.03
33				
34	9.8	9.49	7.77	7.82
35				
36				
37	10.13	9.94	8.82	7.7
38				
39	9.87	9.52	8.25	7.94
40				
41	9.81	9.59	8.45	7.7
42				
43	9.53	9.55	8.23	7.3

Appendix Table B7 (Continued)

Days of operation	R1 pH	R2 pH	R3 pH	Feed water pH
44				
45				
46	9.45	9.28	8.36	8.1
47				
48	9.55	9.44	8.5	7.44
49				
50	9.57	9.63	8.4	7.56
51				
52				
53				
54	9.49	9.5	8.43	6.17
55				
56	9.44	9.61	8.2	7.1
57				
58				
59				
60				
61	9.21	9.25	7.98	6.89
62				
63	9.44	9.3	8.44	6.68
64				
65	9.63	9.51	8.38	7.16
66				
67	9.36	9.37	8.55	7.16
68				
69	9.66	9.46	8.51	6.89
70				
71	9.45	9.38	8.75	6.8
72				
73				
74	9.51	9.53	8.81	7.03

Appendix Table B8 Phase 3 raw data: VFA analysis of leachate

Days of operation	R1 VFA concentration (mg/l)	R2 VFA concentration (mg/l)	R3 VFA concentration (mg/l)
0			
1			
2			
3			
4			
5			
6			
7			
8			
9			
10			
11	3975	3900	3750
12	4185	5460	5400
13			
14	3375	4365	2340
15			
16	3750	4462.5	3750
17			
18			
19			
20	5812.5	4893.75	3750
21			
22			
23			
24	6937.5	5850	5175
25			
26			
27			
28	6412.5	6281.25	6150
29			
30			
31			
32	6956.25	6168.75	6525
33			
34	7162.5	5850	5887.5
35			
36			
37	6300	5850	5925
38			
39	6675	6412.5	6300
40			
41	6637.5	5700	6543.75
42			
43	7425	5775	6075

Appendix Table B8 (Continued)

Days of operation	R1 VFA concentration (mg/l)	R2 VFA concentration (mg/l)	R3 VFA concentration (mg/l)
44			
45			
46	5730	5400	4170
47			
48	5775	4500	6712.5
49			
50	6543.75	7462.5	9637.5
51			
52			
53			
54	6975	5287.5	5212.5
55			
56	7800	7518.75	8981.25
57			
58			
59			
60			
61	4950	5062.5	5100
62			
63	8400	6000	9975
64			
65	8250	6150	8193.75
66			
67	10050	6712.5	7237.5
68			
69	8212.5	6225	7912.5
70			
71	9937.5	10050	12337.5
72			
73			
74	9375	11512.5	14587.5

Appendix Table B9 Phase 3: COD analysis of leachate

Days of operation	R1 COD concentration (mg/l)	R2 COD concentration (mg/l)	R3 COD concentration (mg/l)
0			
1			
2			
3			
4			
5			
6			
7			
8			
9			
10			
11	11200	10800	10800
12	11200	11600	10800
13			
14			
15	10800	12800	12800
16			
17			
18	11200	10400	11200
19			
20	11200	18400	9600
21	11200	10800	10400
22			
23			
24	11200	11200	10400
25			
26			
27			
28	12400	11200	7200
29			
30			
31			
32	12400	13600	12800
33	18000	14000	13600
34			
35			
36			
37	11200	12800	11200
38			
39	15200	12800	15200
40			
41	12800	11200	12800
42			
43	10400	9600	10400

Appendix Table B9 (Continued)

Days of operation	R1 COD concentration (mg/l)	R2 COD concentration (mg/l)	R3 COD concentration (mg/l)
44			
45			
46	10400	10800	10400
47			
48	11200	11600	9200
49			
50	12000	12800	12800
51			
52			
53			
54	10800	12400	12800
55			
56	11200	14400	14400
57			
58			
59			
60			
61	12800	13600	13600
62			
63	13600	13600	15200
64			
65	14400	14000	14000
66			
67	13600	13600	13600
68			
69	13600	15200	20000
70			
71	14400	15200	16000
72			
73			
74	13600	16000	14400

Appendix Table B10 Phase 3 raw data: TDS analysis of leachate

Days of operation	R1 TDS concentration (mg/l)	R2 TDS concentration (mg/l)	R3 TDS concentration (mg/l)
0			
1			
2			
3			
4			
5			
6			
7			
8			
9			
10			
11	14945	12215	13745
12	13030	13210	13745
13			
14	16355	19125	15945
15	18070	18010	18845
16			
17			
18			
19			
20	14880	15205	11960
21	15405	16720	15235
22			
23			
24	22370	17550	20180
25			
26	19530	22495	19035
27			
28	18680	16810	15945
29			
30			
31			
32	19835	19785	19515
33			
34	24960	20690	18765
35			
36			
37	22565	18105	17395
38			
39	19320	14330	17760
40			
41	20360	14355	15655
42			
43	25450	19500	19395

Appendix Table B10 (Continued)

Days of operation	R1 TDS concentration (mg/l)	R2 TDS concentration (mg/l)	R3 TDS concentration (mg/l)
44			
45			
46	16710	15980	17335
47			
48			
49			
50	17140	13240	19750
51			
52			
53			
54	16800	14785	16405
55			
56	17010	13250	21205
57			
58			
59			
60			
61	20440	10330	13210
62			
63	19105	16340	21335
64			
65	21115	16990	14200
66			
67	18810	14435	16040
68			
69	21325	16785	17470
70			
71	22795	23425	27360
72			
73			
74			

Appendix C
Gas Analysis Raw Data

Appendix Table C1 Phase 2 raw data: Gas production measurement

Days of operation	R1 Gas production (ml)	R2 Gas production (ml)	R3 Gas production (ml)
0	0	0	0
1	0	0	0
2	0	0	0
3	0	0	0
4	0	0	0
5	0	0	0
6	0	0	0
7	0	0	0
8	0	0	0
9	0	0	0
10	0	0	0
11	0	0	0
12	0	0	0
13	0	0	0
14	0	0	0
15	0	0	0
16	0	0	0
17	0	0	0
18	0	0	0
19	0	0	0
20	0	0	0
21	0	0	0
22	0	0	0
23	0	0	0
24	0	0	0
25	0	0	0
26	0	0	0
27	0	0	0
28	270	0	0
29	0	0	0
30	0	0	0
31	0	0	0
32	0	0	0
33	0	0	0
34	0	0	0
35	0	0	0
36	0	0	0
37	0	0	0
38	0	75	0
39	0	0	100
40	0	0	0
41	0	0	0
42	0	0	0
43	0	0	0

Appendix Table C1 (Continued)

Days of operation	R1 Gas production (ml)	R2 Gas production (ml)	R3 Gas production (ml)
44	0	0	0
45	130	85	190
46	0	100	0
47	90	110	100
48	170	75	85
49	0	275	125
50	0	0	0
51	0	0	0
52	0	0	0
53	0	0	0
54	0	0	0
55	0	0	0
56	0	0	0
57	0	0	0
58	0	0	0
59	0	0	0
60	0	0	0
61	0	45	0
62	0	0	0
63	160	85	155
64	0	70	0
65	0	0	250
66	0	0	0
67	0	0	0
68	150	295	310
69	130	0	0
70	320	325	340
71	0	0	0
72	0	0	0
73	0	0	0
74	115	220	165
75	180	115	190
76	0	0	0
77	0	0	0
78	0	0	0
79	0	0	0
80	150	100	55
81	90	55	0
82	110	90	100
83	0	0	0
84	80	30	30
85	0	0	0
86	150	100	80
87	0	0	0
88	150	145	0
89	210	175	275

Appendix Table C2 Phase 3 raw data: Gas production measurement

Days of operation	R1 Gas production (ml)	R2 Gas production (ml)	R3 Gas production (ml)
0	0	0	0
1	100	0	125
2	0	0	00
3	250	0	0
4	180	0	120
5	0	75	80
6	0	0	0
7	190	130	170
8	210	200	0
9	0	0	0
10	0	0	0
11	350	165	20
12	160	225	0
13	110	45	0
14	145	200	75
15	260	260	150
16	260	185	100
17	0	0	0
18	350	225	80
19	0	0	0
20	160	250	0
21	370	300	250
22	230	40	50
23	0	0	0
24	290	170	40
25	250	120	110
26	300	200	160
27	0	0	0
28	310	185	0
29	0	0	0
30	0	0	0
31	0	0	0
32	300	160	160
33	250	100	100
34	210	35	0
35	0	0	0
36	120	0	0
37	0	85	0
38	0	0	0
39	470	215	80
40	0	0	0
41	420	150	200
42	0	0	0
43	270	160	100

Appendix Table C2 (Continued)

Days of operation	R1 Gas production (ml)	R2 Gas production (ml)	R3 Gas production (ml)
44	0	0	0
45	0	0	0
46	410	280	100
47	0	0	0
48	280	260	190
49	0	0	0
50	300	230	190
51	0	0	0
52	0	0	0
53	0	0	0
54	340	215	230
55	0	0	0
56	270	280	190
57	60	40	85
58	0	0	0
59	0	0	0
60	260	120	120
61	170	250	220
62	0	110	110
63	280	250	270
64	0	0	0
65	0	0	250
66	0	0	0
67	190	190	320
68	0	0	0
69	100	90	270
70	0	0	0
71	300	70	290
72	0	0	0
73	0	0	0
74	300	170	280

Note** measurement taken by water displacement volumetric gas analysis

Appendix Table C3 Phase 3: GC6890 Agilent Gas chromatography raw data

	Retention time (min)	Area	Factor	A x F	% gas
Sample 1	0.418	459.50	(CH4)1.255	576.67	5.82
Reactor 1	1.502	331.42	(O2) 0.478	158.42	1.60
	1.736	19128.20	(N) 0.478	9167.18	92.58
Sample 2	0.420	380.16	(CH4)1.255	477.1	4.93
Reactor 1	1.513	429.16	(O2) 0.478	205.14	2.12
	1.750	18800	(N) 0.478	8986.4	92.94
Sample 3	0.415	414.63	(CH4)1.255	520.36	5.37
Reactor 1	1.505	375.20	(O2) 0.478	179.34	1.85
	1.746	18804.60	(N) 0.478	8988.60	92.78
Sample 4	0.412	490.56	(CH4)1.255	615.65	6.08
Reactor 1	1.504	340.08	(O2) 0.478	162.56	1.61
	1.740	19552.60	(N) 0.478	9346.14	92.31
Sample 1	0.413	689.96	(CH4)1.255	865.90	9.17
Reactor 2	1.505	411.64	(O2) 0.478	196.77	2.08
	1.742	17536.20	(N) 0.478	8382.30	88.75
Sample 2	0.418	772.94	(CH4)1.255	970.04	9.86
Reactor 2	1.512	401.56	(O2) 0.478	191.95	1.95
	1.756	18161	(N) 0.478	8680.96	88.19
Sample 3	0.439	885.13	(CH4)1.255	1110.83	11.09
Reactor 2	1.564	314.03	(O2) 0.478	150.11	1.50
	1.835	18310.40	(N) 0.478	8752.37	87.41
Sample 4	0.436	948.04	(CH4)1.255	1189.78	11.52
Reactor 2	1.566	360.78	(O2) 0.478	172.46	1.67
	1.825	18752.6	(N) 0.478	8963.74	86.81
Sample 1	0.423	924.38	(CH4)1.255	1160.10	11.84
Reactor 3	1.530	474.80	(O2) 0.478	226.95	2.32
	1.735	17600	(N) 0.478	8412.8	85.85
Sample 2	0.415	1446.34	(CH4)1.255	1815.15	17.58
Reactor 3	1.528	344	(O2) 0.478	164.43	1.59
	1.788	17458.9	(N) 0.478	8345.35	80.83
Sample 3	0.424	1651.41	(CH4)1.255	2072.52	21.03
Reactor 3	1.514	298.58	(O2) 0.478	142.72	1.45
	1.810	15981.8	(N) 0.478	7639.3	77.52

Phase 3: GC6890 Agilent gas chromatography summary

Reactor 1 avg. Methane = 5.55 % or 541.65 ml
Reactor 1 avg. Oxygen = 1.79 % or 175.06 ml
Reactor 1 avg. Nitrogen = 92.65 % or 9038.29 ml

Reactor 1 Phase 3 total gas volume = 9775 ml

Reactor 2 avg. Methane = 10.41 % or 669.87 ml
Reactor 2 avg. Oxygen = 1.8 % or 115.87 ml
Reactor 2 avg. Nitrogen = 87.79 % or 5649.26 ml

Reactor 2 Phase 3 total gas volume = 6435 ml

Reactor 3 avg. Methane = 16.82 % or 897.16 ml
Reactor 3 avg. Oxygen = 1.79 % or 95.26 ml
Reactor 3 avg. Nitrogen = 81.40 % or 4342.58 ml

Reactor 3 Phase 3 total gas volume = 5335 ml

Appendix D
International Conference on Environmental Science and Development, 2010

2010 IACSIT SINGAPORE CONFERENCES SCHEDULE

The 2010 International Conference on Agricultural and Animal Science (CAAS 2010)
The 2010 International Conference on Chemical Engineering and Applications (CCEA 2010)
The 2010 International Conference on Cellular and Molecular Biology Science (CMBS 2010)
The 2010 International Conference on Environmental Science and Development (CESD 2010)
The 2010 International Conference on Forestry Applications and Development (CFAD 2010)
The 2010 International Conference on Earth Engineering and Science (EES 2010)
The 2010 International Conference on Sustainable Design and Construction Engineering (SDCE 2010)

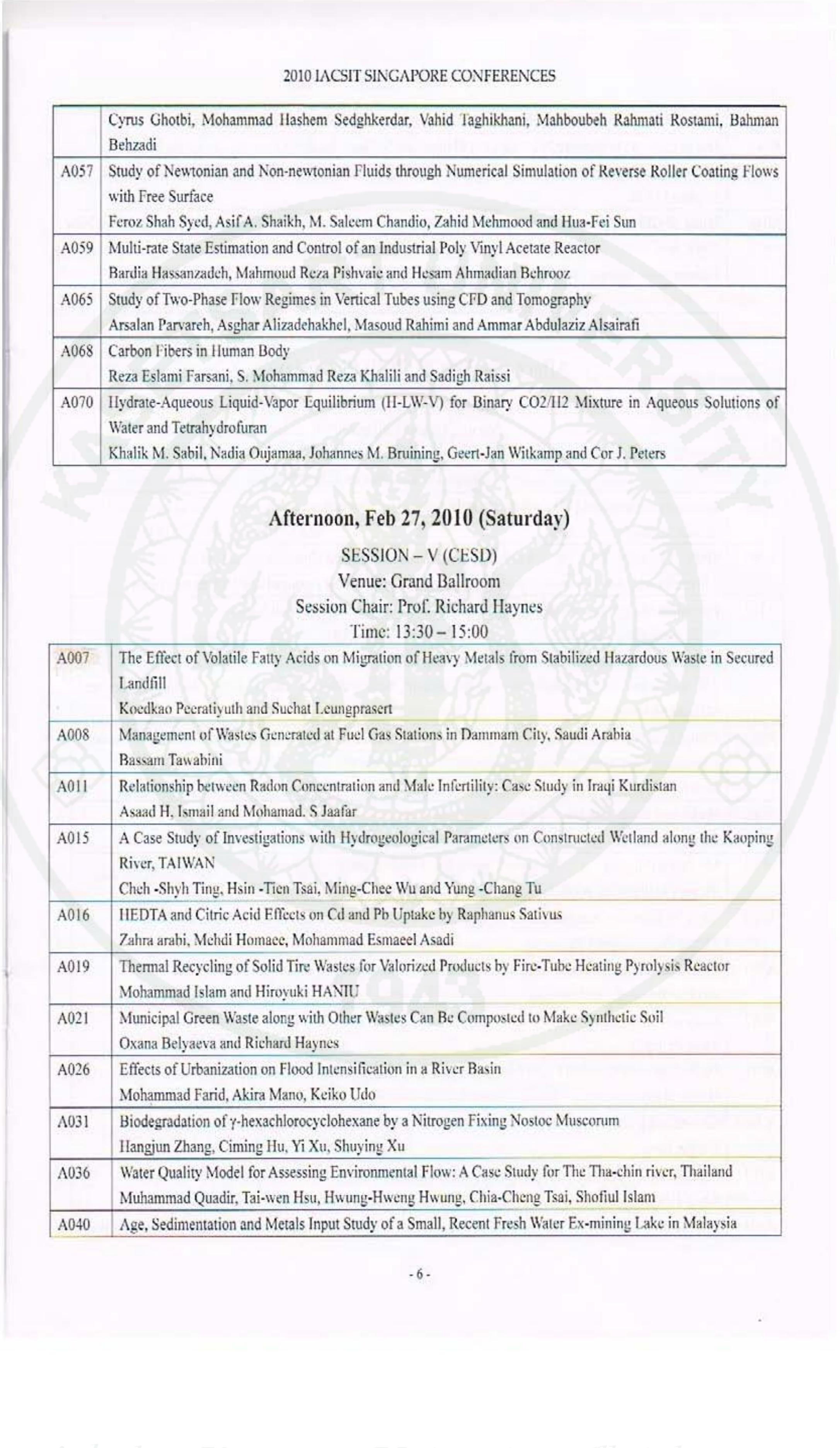
Quality Hotel, Singapore

Feb 26 - 28, 2010

Sponsored and Published by

IACSIT
WWW.IACSIT.ORG
CBEES
www.cbees.org
ACADEMIC
ACES
FAS
BBES

www.iacsit.org
www.cbees.org



	Cyrus Ghotbi, Mohammad Hashem Sedghkerdar, Vahid Taghikhani, Mahboubeh Rahmati Rostami, Bahman Behzadi
A057	Study of Newtonian and Non-newtonian Fluids through Numerical Simulation of Reverse Roller Coating Flows with Free Surface Feroz Shah Syed, Asif A. Shaikh, M. Saleem Chandio, Zahid Mehmood and Hua-Fei Sun
A059	Multi-rate State Estimation and Control of an Industrial Poly Vinyl Acetate Reactor Bardia Hassanzadeh, Mahmoud Reza Pishvaie and Hesam Ahmadian Behrooz
A065	Study of Two-Phase Flow Regimes in Vertical Tubes using CFD and Tomography Arsalan Parvareh, Asghar Alizadehakhel, Masoud Rahimi and Ammar Abdulaziz Alsairafi
A068	Carbon Fibers in Human Body Reza Eslami Farsani, S. Mohammad Reza Khalili and Sadigh Raissi
A070	Hydrate-Aqueous Liquid-Vapor Equilibrium (H-LW-V) for Binary CO2/H2 Mixture in Aqueous Solutions of Water and Tetrahydrofuran Khalik M. Sabil, Nadia Oujamaa, Johannes M. Bruining, Geert-Jan Witkamp and Cor J. Peters

Afternoon, Feb 27, 2010 (Saturday)

SESSION – V (CESD)
Venue: Grand Ballroom
Session Chair: Prof. Richard Haynes
Time: 13:30 – 15:00

A007	The Effect of Volatile Fatty Acids on Migration of Heavy Metals from Stabilized Hazardous Waste in Secured Landfill Koedkao Peeratiyuth and Suchat Leungprasert
A008	Management of Wastes Generated at Fuel Gas Stations in Dammam City, Saudi Arabia Bassam Tawabini
A011	Relationship between Radon Concentration and Male Infertility: Case Study in Iraqi Kurdistan Asaad H. Ismail and Mohamad. S Jaafar
A015	A Case Study of Investigations with Hydrogeological Parameters on Constructed Wetland along the Kaoping River, TAIWAN Cheh -Shyh Ting, Hsin -Tien Tsai, Ming-Chee Wu and Yung -Chang Tu
A016	HEDTA and Citric Acid Effects on Cd and Pb Uptake by Raphanus Sativus Zahra arabi, Mehdi Homaee, Mohammad Esmaeel Asadi
A019	Thermal Recycling of Solid Tire Wastes for Valorized Products by Fire-Tube Heating Pyrolysis Reactor Mohammad Islam and Hiroyuki HANIU
A021	Municipal Green Waste along with Other Wastes Can Be Composted to Make Synthetic Soil Oxana Belyaeva and Richard Haynes
A026	Effects of Urbanization on Flood Intensification in a River Basin Mohammad Farid, Akira Mano, Keiko Udo
A031	Biodegradation of γ-hexachlorocyclohexane by a Nitrogen Fixing Nostoc Muscorum Hangjun Zhang, Ciming Hu, Yi Xu, Shuying Xu
A036	Water Quality Model for Assessing Environmental Flow: A Case Study for The Tha-chin river, Thailand Muhammad Quadir, Tai-wen Hsu, Hwung-Hweng Hwung, Chia-Cheng Tsai, Shofiul Islam
A040	Age, Sedimentation and Metals Input Study of a Small, Recent Fresh Water Ex-mining Lake in Malaysia

Certificate for Participation

This is to certify that MR. KOEDKAO PEERATIYUTH, from KASETSART UNIVERSITY has attended, and delivered an oral presentation in the 2010 International Conference on Cellular and Environmental Science and Development (CESD 2010) in Singapore during February 26-28, 2010.

Conference Chair
CESD, 2010

ISBN 978-1-84626-024-7
Proceedings of 2010 International Conference on Environmental Science and Development (CESD 2010)
Singapore, 26-28 February, 2010

The Effect of Volatile Fatty Acids on Migration of Heavy Metals from Stabilized Hazardous Waste in Secured Landfill

Koedkao Peeratiyuth[1] and Suchart Leungprasert[2 +]

[1] *Master student, Department of Environmental Engineering, Faculty of Engineering, Kasetsart University, Thailand*

[2]*Lecturer, Department of Environmental Engineering and National Center of Excellence for Environmental and Hazardous Waste Management, Faculty of Engineering, Kasetsart University, Thailand*

Abstract. Although hazardous waste was stabilized and solidified with cement-lime process, it has still found some heavy metals and organic contents with very high concentrations in leachate from the secured landfill in Thailand. Due to Thailand's regulation, hazardous waste is required to stabilize before disposal in the landfill. This situation is not usual because normally at pH of 12 any microbial activity should be inhibited resulting no organic concentration or its end products found in the leachate. However, this finding led to this research topic on the end product occurring from microbial activity affecting heavy metals leaching. In this research, the end product was volatile fatty acid generated from secured landfill reactor. A variation of the amount of volatile fatty acid may affect the leaching of heavy metals in the stabilized waste. The experiments were done in the batch scale anaerobic landfill reactor operating for 120 days. The goal of this research is to investigate the effect of volatile fatty acid variation on heavy metals leaching in the stabilized hazardous waste.

The experiments were divided into two phases. The first phase was the batch experiment used to find the effect of variation of volatile fatty acids on heavy metal leaching. In this experiment, the stabilized hazardous waste samples from secured landfill were added with acetic acid produced from acidogenic bacteria activity[1]. Ten grams of each sample were added in the Erlenmeyer flask with 100ml of acetic acid following the Toxicity Characteristic Leaching Procedure (TCLP) and it was shaken at 30 rpm for 18 hours. The liquid samples were then separated from solid. They were digested under acid condition and analyzed by the Atomic Absorption Spectrometer to measure heavy metal contents. The results showed that leaching of heavy metals increased when the addition amount of acetic acids increased.

The second phase experiments were done by adding the stabilized hazardous waste sample into the anaerobic landfill reactor with the approximately effective volume of 24 liter. The microbial activity was indicated by determining the gas production, volatile fatty acid generation and volatile solid reduction. The variation of pH from the leachate was determined. Moreover, dominant heavy metals were analyzed from the leachate and residual stabilized waste. The results showed that the total organic carbon (TOC) and volatile solids from the stabilized waste before adding to the landfill reactors were 5.4 mg/g sample and 5.0 mg/g sample, respectively. For reactor 1,2 and 3, the initial pH were 12.32, 11.28, 10.50, respectively and the total heavy metals including Cr, Ni, Pb and Cd were 6.89 mg/g, 30.78 mg/g, 40.709 mg/g, respectively. During the operation, volatile fatty acid produced from the reactors were range from 3,000 mg/l to 9,000 mg/l. Compare to the total organic content, it was found that VFA produced was about 5.38 % in the reactor (0.92 kg TOC or 1.25 L from 23.29L total). The gas emissions from the reactors were quite low at the beginning of experiment setup. At the day 40, gas production increased rapidly for about 30-50 ml/day. From these experiments, it was found that at the initial pH of 12.3, the microorganisms has been survived and can degrade some organic content. As a result, the heavy metals detected from the leachate were increased during the secured landfill reactor operation.

Keywords: stabilized hazardous waste, acidogenic bacteria activity, anaerobic landfill reactor, volatile fatty acid, heavy metals

---

[+] Corresponding author. Tel.: + (662-9428555 ext 1027); fax: +(662-5790730).

E-mail address: (fengscl@ku.ac.th).

CURRICULUM VITAE

NAME : Mr. Koedkao Peeratiyuth

BIRTH DATE : February 9, 1985

BIRTH PLACE : Bangkok, Thailand

EDUCATION :

YEAR	**INSTITUTE**	**DEGREE/DIPLOMA**
2002	SIIT, Thammasat Univ.	B.Eng. (Industrial)
2007	Kasetsart Univ.	M.Eng. (Environmental)