CHAPTER 3

METHODOLOGY

3. 1 Materials and methods

3.1. 1 Configuration of the simulated landfill reactors

The three simulated landfill reactors were constructed using a PVC pipe. Each reactor had a diameter of 0.4 m and a height of 0.7 m. The columns were assembled with two 0.5 m outer diameter PVC flanges at both ends to provide support for top and bottom lids. A coating of Silicone was applied to the interior and exterior of the flanged joints to ensure that the junctions would be water and gas tight. The design and operation features of the simulated landfill reactor with recycling are shown in Figure 5. One simulated landfill reactor is taken as a control and is operated as in Jaijongruk (2004).

The reactors were equipped with three ports, one port was used for leachate drainage and sampling while the other two inlet/outlet ports were placed at the top lid to collect gas samples and to add liquid by using a distribution system made of PVC. A 2 cm diameter hole at the center of the bottom lid facilitated the installation of a leachate collection pipe. A 2 to 1 cm PVC reducer with a PVC tee was connected to a leachate collection pipe. The tee attached to 1 cm diameter Tygon® tube which was used to transfer leachate to a 27 L acelic container or to a leachate sampling port.

A 2 cm diameter hole at the center of the top lid and 1 cm diameter hole located 14 cm radially apart from the center hole functioned as liquid addition and gas sampling ports, respectively. A 2 cm diameter PVC pipe connected with a 2 to 1 cm PVC reducer and 1 cm Tygon® tube was used for liquid addition. A PVC tee was placed on another hole. One end of the tee was attached by 1 cm Tygon® tube. The tube was connected to the leachate container and functioned as a pressure balance and

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gas collection line, whereas, the other end of the tee was capped by rubber septum and functioned as a gas sampling port.

Landfill gas produced in the reactors was collected and measured by an inverted glass cylinder method. This technique utilized one 1-L glass cylinder placed invertly in 2-L glass cylinder which was filled with confining solution (20% Na_2SO_4 in 5 % H_2SO_4) (Sawyer and McCarty, 1989). The inner cylinder was lifted until the level of the confining solution in both cylinder equilibrated, and the amount of gas produced in a certain period was indicated by the volume occupied by gas in the inner cylinder.

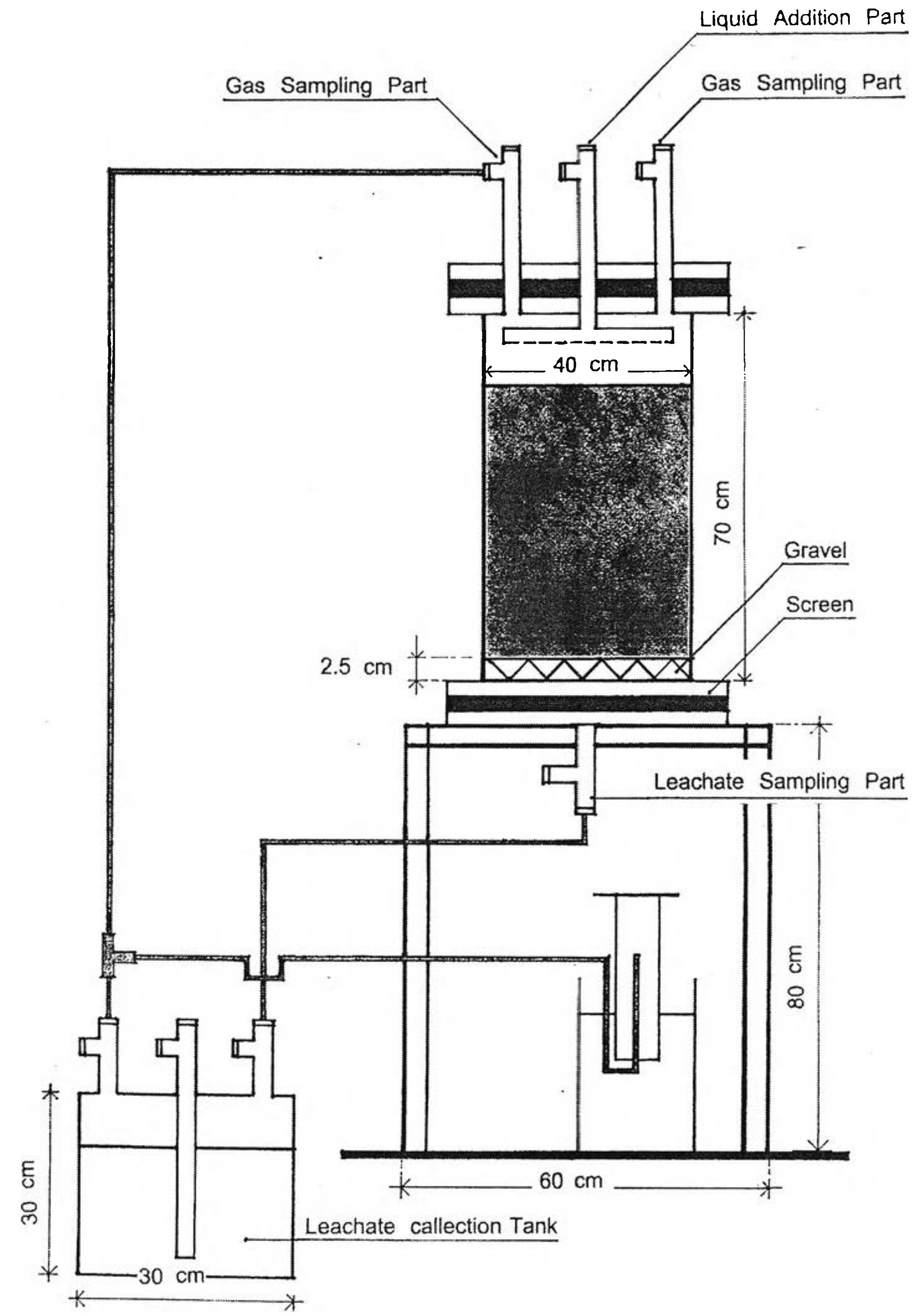

Figure 3.1 Design and operational features of the reactor with leachate recycle.

3.1.2 Characteristics of waste matrix

Each reactor is loaded with 20 kg of solid waste prepared, shredded and compacted solid waste mixture and 1 L of anaerobic digested sludge obtained from wastewater treatment plant. The simulated solid waste mixture representing typical solid waste composition of Sri-Mum-Muan Market and consists of 80% vegetables and 20% fruit by weight. Shredded refuse of composition presented in Table 7 wasl mixed prior to loading. Preliminary analysis of waste samples was indicated solid waste moisture content, volatile solid content and elemental analyses for C, H, O, N, and S.

Table 3.1 Solid wastes compositions

Type	Total weight (wet) (kg)	Percent (by weight)
Chinese White Cabbage	2.5	12.5
Morning Glory	2.3	11.5
Eggplant	6.3	31.5
Kale	2	10
Cow Pea	2.5	12.5
Water Mimosa	0.6	3
Cabbage	0.6	3
Chinese Cabbage	0.4	2
Bitter Cucumber	0.5	2.5
Banana	1	5
Orange	1.3	6.5
Total	20	100

3.1.3 Sludge Seeding

To facilitate initiation of methane fermentation, sludge from a digested sludge sample obtained from an anaerobic digester at the Utility Business Alliance Co., Ltd. was added to three simulated landfill reactors. The seeding sludge characteristics are presented in Table 3.2. This seeding procedure would be initiated on refuse loading day. Each reactor was added with 1 L of anaerobic digester sludge. In addition, the 2, 0.6, 0.6, and 1 L of sludge seeding were added on the top of reactor in each of the three simulated landfill reactors on Day 125, 142, 143, and 146, respectively by using anaerobic digester sludge from HuayWang Wastewater Treatment Plant, Bangkok. The characteristics of seed sludge are presented in Table 3.3. The seeded sludge was mixed with the recirculated leachate before the addition to enhance distribution.

Table 3.2 Analysis of the digested sludge added to all three simulated landfill reactors during seeding

Parameter	Analysis
Chemical oxygen demand, mg/L	2,300
Total solids, mg/L	1,000
Total Volatile solids, mg/L	126
Alkalinity, mg/L as $CaCO_3$	1,550
pH	7.73

Table 3.3 Analysis of the digested sludge added to all three simulated landfill reactors during operation

Parameter	Analysis
Chemical oxygen demand, mg/L	41,600
Total solids, mg/L	31,654
Total Volatile solids, mg/L	126
Alkalinity, mg/L as $CaCO_3$	720
pH	7.43

3.1.4. Leachate recirculation phase shift conditions

For this experiment, all simulated landfill reactors was used leachate recirculation phase shift conditions of Turajane (2001) as guideline because of similarity in amounts and type of refuse. Leachate recirculation plan for this experiment was divided five operational phases based on percent methane production. The five operational phases are shown on Table 3.4. The shift of each phase was depending on parameter of average percent methane production.

Table 3.4 Leachate recirculation phase shift conditions for three simulated landfill reactors

Phase	Range % CH4	Leachate Recycle Volume
1	0-15	0% of total moisture in system
2	16-19	5% of total moisture in system
3	20-29	15% of total moisture in system
4	30-40	25% of total moisture in system
5	≥40	25% of total moisture in system

3.1.5. Addition of Selected Heavy Metals

This experiment consists of three stimulated landfill reactors. In the first reactor (Reactor 1), is operated with nickel and zinc added during acidogenic phase. The second reactor (Reactor 2), is operated with nickel and zinc added during methanogenic phase. The last one is the control reactor operated without nickel and zinc added (Jaijongrak, 2004), the acid formation phase was established in first reactor. Nickel and zinc were loaded in the reactor according to directives of the Turkish Hazardous Waste Control Regulations. Two heavy metals (Ni, Zn) were selected based on two criteria:

1. general presence in municipal refuse;
2. listed as hazardous waste or toxic by RCRA;

Additions of heavy metals were performed to reactors 1 and 2 to see effects of inhibition on stabilization and leaching potential of nickel and zinc. The amounts introduced followed the directives of the Turkish Hazardous Waste Control Regulations since it still allows for co-disposal practice.

The second column of the table 3.5 indicates the total amounts of nickel and zinc added to the reactors according to the Turkish Hazardous Waste Control Regulations.

Table 3.5 Masses of the nickel and zinc loadings into the reactors[a].

Selected heavy metals and their salts	Metals (g)	Metal salts (g)	Regulations[c] (g/t MSW)[b]
Ni/$NiCl_2 6H_2O$	2	8.09	100
Zn/$ZnCl_2$	2	4.16	100

[a] g metal/kg wet shredded municipal solid waste
[b] MSW: municipal solid waste.
[c] allowable amount according to Turkish Hazardous waste Control Regulations.

3.1.6 Simulated landfill reactors operation

3.1.6.1 Moisture Applications and Management

Preliminary analyses indicated that the synthetic solid waste had approximately 90% of moisture content. The liquid collected at the bottom of each reactor on the next day will be recycled to the top of reactor. This water application procedure was repeated until the amount of liquid introduced each day, would equal to the amount of liquid collected on the next day. This date was then defined as Day

0, or when indicated field capacity was reached and leachate production began. A sample of leachate from each cell was collected at that time and analyzed for all indicator parameters.

There was no moisture addition to all recycle reactors from August 15, 2003 (Day 0) to October 16, 2003 (Day 63), since the volume of deionized water previously added was determined sufficient to initiate microbial active. The deionized water volume of approximately 0.5 L was applied to all reactors on October 16, 2003 (Day 63), October 18, 2003 (Day 65), October 22, 2003 (Day 69) and October 24, 2003 (Day 71) for make up volumes of moisture that was leached out for sampling purposes.

3.1.6.2 Operation

For this experiment, methane percentages as main indicator for changing of phase in landfill stabilization. The methane fermentation phase was started when the initial methane concentration was approximately 40%.

Reactor 1: Addition of nickel and zinc during acidogenic phase in Reactor 1

The leachate recirculation volume of approximately 1,000 mL was applied to the recycle reactor from Day 148 to Day 151. On day 152, the acidogenic formation phase was established in first reactor and Nickel and zinc was loaded in the reactor in the form of solution.This reactor was started recycle ratio about 5% of total moisture in system. The leachate recirculation volume of approximately 900 mL/day was applied to the reactor from Day 152 to Day 165. The recirculation rate was change to 1,200 mL/day (7% of total moisture in system) for a short period from Day 166 to Day 171 and on Day 172 to Day 193, increased to 2,700 mL/day (15% of total moisture in system) with buffer addition to maximize the gas production rate. After that the recirculation leachate was change to 4,500 mL/day (25% of total moisture in system) from Day 194 until the end of the reactor experiment on Day 195. The pH of recycled leachate was neutralized with 5 N NaOH to bring the pH up to 7.0 prior to leachate introduction back to the reactor.

Reactor 2: Addition of Nickel and Zinc during Methanogenic phase in Reactor 2.

The leachate recirculation volume of approximately 1,000 mL was applied to the recycle reactor from Day 148 to Day 151. This reactor was started with recycle ratio about 5% of total moisture in system. The leachate recirculation volume of approximately 900 mL/day was applied to the reactor from Day 152 to Day 165. The recirculation rate was change to 1,200 mL/day (7% of total moisture in system) for a short period from Day 166 to Day 171 and on Day 172 to Day 178 increased to 2,700 mL/day (15% of total moisture in system). In the second reactor, after the onset of methanogenic indicateing that condition reflecting high gas production and low COD concentration and methane percentage about 40% (Day 181). Then Nickel and zinc was loaded in the reactor. During the last operating period (Day 179 to Day 195), 4,500 mL/day (25% of total moisture in system) of leachate recirculation was applied to the reactor. The pH of recycled leachate was neutralized with 5 N NaOH to bring the pH up to 7.0 prior to leachate introduction back to the reactor.

Reactor 3: Control Reactor (Jaijongruk, 2004).

The leachate recirculation volume of approximately 1,000 mL was applied to the recycle reactor from Day 148 to Day 151. This reactor was started with recycle ratio about 5% of total moisture in system. The leachate recirculation volume of approximately 900 mL/day was applied to the reactor from Day 152 to Day 165. The recirculation rate was change to 1,200 mL/day (7% of total moisture in system) for a short period from Day 166 to 171. From Day 172 to Day 180, 2,700 mL/day (15% of total moisture in system) of leachate recirculation was applied in to reactor. During the last operating period, Day 181 to Day 193, the recirculation volume applied to reactor was 4,500 mL/day (25% of total moisture in system). The pH of recycled leachate was neutralized with 5 N NaOH to bring the pH up to 7.0 prior to leachate introduction back to the reactor.

3.1.7 Sampling and Analytical Protocols

The collected leachate and gas samples will be monitored on a regular basis to track fate of selected heavy metals and their effects on solid waste stabilization. The quality and quantity of gas and leachate varied as different phases of stabilization occurred. Therefore, monitoring for changes in parameters indicative of landfill stabilization was used to identify the sequential phases of solid waste degradation.

Leachate samples were collected from the bottom of the recycle reactors, and were analyzed for chemical oxygen demand (COD), pH, oxidation-reduction potential (ORP), orthophosphate, ammonia nitrogen, sulfide, sulfate, alkalinity and heavy metals. The daily temperature, daily gas production rate, and gas composition were also observed. Gas composition, measured as percent by volume, was determined for methane. Detail about frequency and method of analyses are listed in Table 3.7.

3.1.7.1 Gas Analysis

The gas produced by the simulated landfill reactors was collected and analyzed for quantity and composition. The amount of gas was measured using inverted glass cylinder method. The gas composition was analyzed using Gas Chromatograph (GC) (19091P-MS4) equipped with a Thermal Conductivity Detector (TCD). The glass packed column used to separate neon, argon, oxygen, nitrogen, methane, carbon monoxide was 30m× 0.32 mm ID. The typical operating conditions for the GC were:

Detector	TCD (Agilent Technology 6890 N Network GC system)
Oven program	40° Isothermal
Sample	250 μL, split (75:1)
Carrier gas	Helium, 2mL/min

Column HP-Molsiv Agilent Technologies
I.D.0.32 mm (widebore)
Length 30 m
Film 12 μm

3.1.7.2 Leachate Analysis

Leachate samples from each of the simulated landfill reactors were collected and characterized for gross parameters and heavy metals.

Leachate Parameters

The leachate parameters included chemical oxygen demand, pH, oxidation-reduction potential (ORP), alkalinity, sulfide, sulfate, ortho-phosphate, ammonia-nitogen. Sulfides were measured periodically to confirm their presence under reducing conditions and nutrients (PO_4 and NH_3N) were also measured to determine sufficiency for biodegradation. pH and ORP were measured with pH meter and ORP meter.

Remaining analyses of leachate parameters were performed according to Standard Methods (Standard Methods for the Examination of Water and Wastewater, 1980) and included:

COD – Chemical oxygen Demand- Titration Method
Total Alkalinity-Titration Method
PO_4^{-3}- Vanadomolybdophosphoric Acid Method
NH_3-N- Kjeldahl Method
Sulfate- Gravimetric Method
Sulfide- Ion Selective Electrode Method

3.1.7.3 Heavy Metals Analysis

Leachate samples were also analyzed for the following metals: Ni, Zn. The concentration of each metal was determined using a Inductive Coupled Plasma (ICP). Everyday 20 mL samples of leachate were acidified to pH 〈 2 with concentrated HNO_3 and stored in polyethylene bottles. These samples were digested prior to total metal determination using a microwave (MILESTONE ETHOS SEL) for leachate samples described in the Appendix D.

Table 3.6 Methods and frequency of simulated landfill leachate parameters analyses

Measurement	Procedure	Frequency
pH	pH meter	Everyday
ORP	ORP meter	Everyday
COD	Standard Methods for water and wastewater Examination # 4500-COD (Titration Method)	Every 2 days
Ammonia-nitrogen	Standard Methods for water and wastewater Examination # 4500- (Kjeldahl Method)	Every month
Ortho-phosphates	Standard Methods for water and wastewater Examination # 4500-P (Vanadomolybophoric Acid Method)	Every month
Sulfides	Standard Methods for water and wastewater Examination # 4500-P (Ion Selective Electrode Method)	Every month
Sulfate	Standard Methods for water and wastewater Examination # 4500-P (Gravimetric Method)	Every month
Alkalinity	Standard Methods for water and wastewater Examination # 4500-P (Titration Method)	Every 2 weeks
Ni, Zn	Inductive Coupled Plasma (ICP)	Everyday of their periods
Gas production	Inverted Glass Cylinder Method	Everyday
Percent Methane	Gas Chromatography (TCD)	Every 3 days

3.1.8 The Simulated Landfill Reactors Disassesembly

On April, 1 2004, the three simulated landfill reactors will be disassembled; leachate will be drained from all reactors for approximately an hour before the disassembly began.