

## CHAPTER 4

### RESULTS AND DISCUSSION



#### 4.1 Reactor Experiment

Graphical representations of the results of analyses performed on leachate and gas samples collected from three simulated landfill cells during the acidogenic phase and methanogenic phases over a period about 195 days are presented in this section and tabulated in Appendices A-G. Day 0 corresponds to August 15, 2003 and it is the time of initial leachate production. Initial leachate concentrations in three simulated landfill reactors prior to the commencement of the experimental study are given in Table 4.1.

**Table 4.1** Initial leachate characteristics of three simulated landfill reactors.

Parameter	pH	ORP <sup>a</sup> (mV)	COD (mg/L)	Alkalinity (mg/L)	Sulfate (mg/L)	Sulfide (mg/L)	PO <sub>4</sub> <sup>3-</sup> - P (mg/L)	NH <sub>3</sub> -N (mg/L)
Reactor 1	3.88	-157.5	44,800	4,100	124	1.2	255	847
Reactor 2	3.90	-197.3	37,466	4,800	162	2.1	245	380
Reactor 3	3.95	-166	36,134	4,000	-	-	204	381

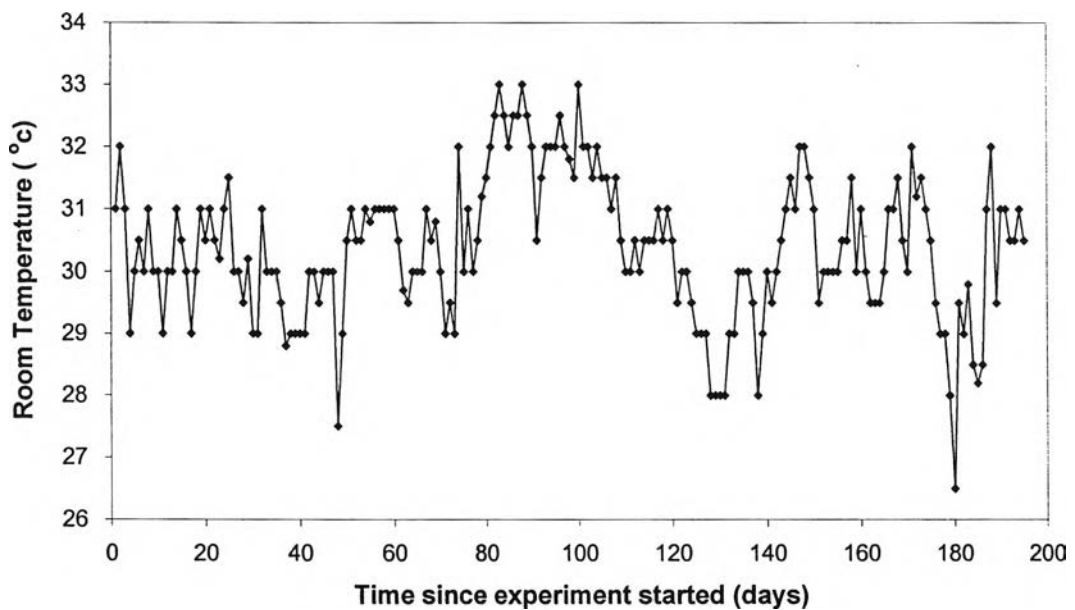
<sup>a</sup> ORP on Day 99

##### 4.1.1 Solid Waste Composition

The organic waste (food waste) from Sri-Mum-Muan Market had an average moisture content of 90%. This was determined from three triplicate samples with respective moisture contents for reactor 1= 90.41 %, reactor 2 = 92.05 %, and reactor 3 = 90.02%. The volatile solids content averaged 90.87% for dried waste. Dry solid wastes for all reactors were also determined for C, H, O, N, S. The results were 50.48% C, 6.05% H, 30.51 %O, 3.40% N, and 0.43% S.

### 4.1.2 Temperature

Ambient room temperature which was moderated by seasonal fluctuations as indicated in Figure 4.1 (Table A-1 in Appendix A). However, temperatures remained between 29 and 32°C throughout majority of the study, with the greatest departure from this range being experienced during the months of November to January.



**Figure 4.1** Temperature of the simulated landfill reactors.

## 4.2 Leachate Analysis

The leachate from the simulated landfill reactors was sampled and analyzed for leachate parameters, and metals. The results of these analyses are presented and discussed in the following section

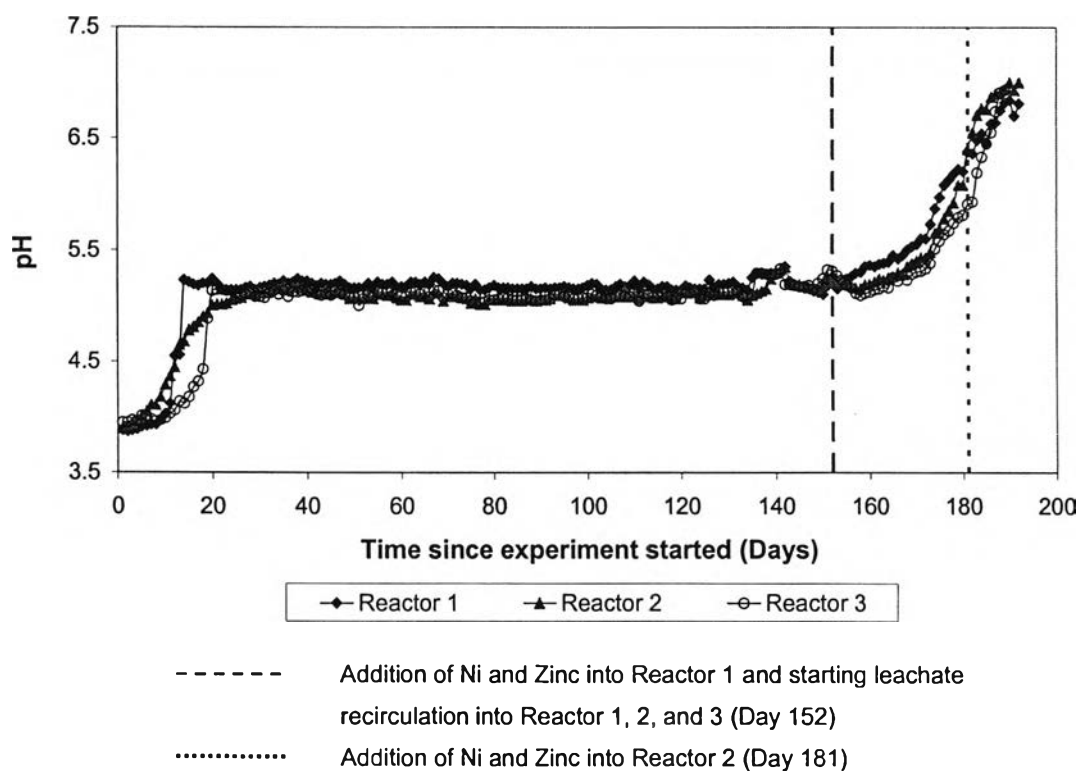
### 4.2.1 pH

The changes in leachate pH are shown in Figure 4.2 (Table B-1 in Appendix B). The initial pH in the reactors 1, 2 and 3 were 3.88, 3.90 and 3.95, respectively. The low initial pH values in all reactors were caused by high amount of moisture

content from vegetable and fruit waste that used as the simulated solid wastes. Thus, it can be produced high amount of acid during degradation process in all reactors.

For reactor 1, the pH increased to 5.23 on Day 14. After Day 14, the pH remained constant between 5.1-5.2 until Day 142. This showed that the methanogenic did not establish well in this reactor. The low pH was typical of the acid formation phase. If the system is totally saturated with acids, the anaerobic methane forming microorganisms may be inhibited and the conversion of VOA to methane will be delayed. Then, sludge seeding was applied to this reactor on Day 125, 142, 143 and 148. This resulted in slight increase in pH values of leachate in this reactor. After metal addition on Day 152, the pH value was slightly decreased in the reactor. Then the leachate recirculation was applied to this reactor. Along with the addition of 5 N NaOH, the pH in system increased to 5.3-7.1 between Day 158 to Day 195.

For reactor 2, the pH throughout the acid formation phase was less than 6.0. After an initial low of 3.9, the pH increased to 5.0 on Day 20. After Day 20, the pH remained constant between 5.0-5.2 until Day 152. This low pH is typical of acid formation phase. The limited number of methane formers originally present in the refuse, the exclusion of soil as a cover material to provide such a seed, and the introduction of air during loading also may have limited the establishment of a viable population of methane formers. Therefore, sludge seeding was applied to this reactor on Day 142. This resulted in slight in pH values in this reactor. On Day 152 to Day 195 the leachate recirculation was applied in this reactor. With the addition of NaOH buffer solution, the pH values rose from 5.2 to near 7 was observed in this reactor. The increase of pH to near neutral was an indicator of methane fermentation on Day 179 until the end of the study.



**Figure 4.2** pH of leachate from the simulated landfill reactors.

For reactor 3, the initial pH value was 3.95, during the first 50 days the pH value was increased from 3.95 to 5.07. Consequently, leachate pH was stable during Day 51 to Day 142. This showed the methanogenic did not establish in this reactor. Therefore, sludge seeding was applied in this reactor to enhance the organic waste stabilization. The pH values were slightly increased in this reactor. On Day 153, the recirculation was applied in the reactor. Since the pH was still not available for the development of a viable methanogenic formation, attempt was made to raise the pH value to near neutral about 7 by 5 N NaOH. This resulted in a rapid increase in pH from Day 152 to Day 195. Leachate recirculation ratio plays an influential role in increasing pH.

The constant pH on Day 50 to Day 142 as shown in Figure 4.2 of both reactors was a result of leak of some parts of reactors. After reactors were renovated, the pH was slightly increased in all reactors. The pH during the final phase of recirculation was beneficial for development of microbial population responsible for waste

stabilization as supported by an abrupt increase in methane percentages and gas generation rates from all recycle reactors. However, the pH levels established were near the neutral range considered necessary for effective anaerobic stabilization of the readily available organic fraction of the refuse contained in all the simulated landfill reactors.

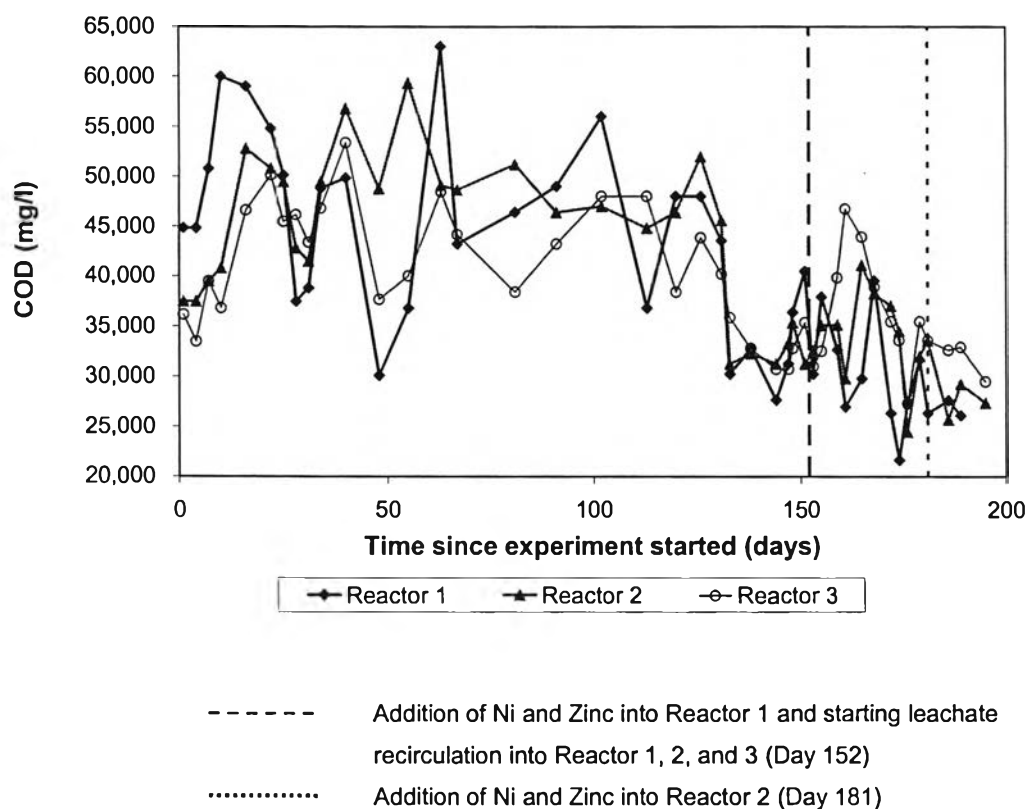
#### 4.2.2 Chemical Oxygen Demand (COD)

The concentration of chemical oxygen demand (COD) indicates the relative organic strength of the leachate generated throughout the phase of landfill stabilization. The results of COD for the simulated landfill reactors are shown in Figure 4.3 (Table B-2 in Appendix B).

The initial COD concentration in the recycle reactors were 44,800 mg/L, 37466 mg/l and 36134 mg/L for reactor 1, 2, and 3, respectively. The leachate COD values were quite fluctuated in all reactors, but the trend was decreased. However, after Day 22, the COD values for the three recycle reactors remained fairly constant at about 48,000-56,000 mg/L for extended period of time. However, on about Day 142, after the systems had been seeded with digested sludge, a slightly decrease in COD to the 32,000-48,000 mg/L range occurred. On Day 152, leachate recirculation was applied in all reactors. The early gradual increase in COD for the recycle reactors around Day 148 to 165 of reactor 2 and 3 was probably due to more complete leaching of the waste mass. Chemical oxygen demand in the leachate from both reactors showed the effect of high rate of leachate recirculation. After the addition of selected heavy metals in Reactor 1 and Reactor 2, COD concentrations in reactor 1 decreased from 40,448 mg/l on Day 151 to 26,112 mg/l on Day 195 and decreased from 33,555 mg/L on Day 181 to 31,948 mg/L on Day 195 in reactor 2 as a result of bacteria leaching activity were decreased.

In terms of conversion of COD (Figure 4.3), leachate from control reactor (Reactor 3) was rapidly depleted in concentration, suggesting a normal sequence of refuse stabilization with some evidence of conversion of less readily available

substrates during the terminal phase. A similar but somewhat delayed pattern of conversion was indicated for reactor 1 and 2 as indicated a definite inhibition of the normal progress of refuse stabilization.

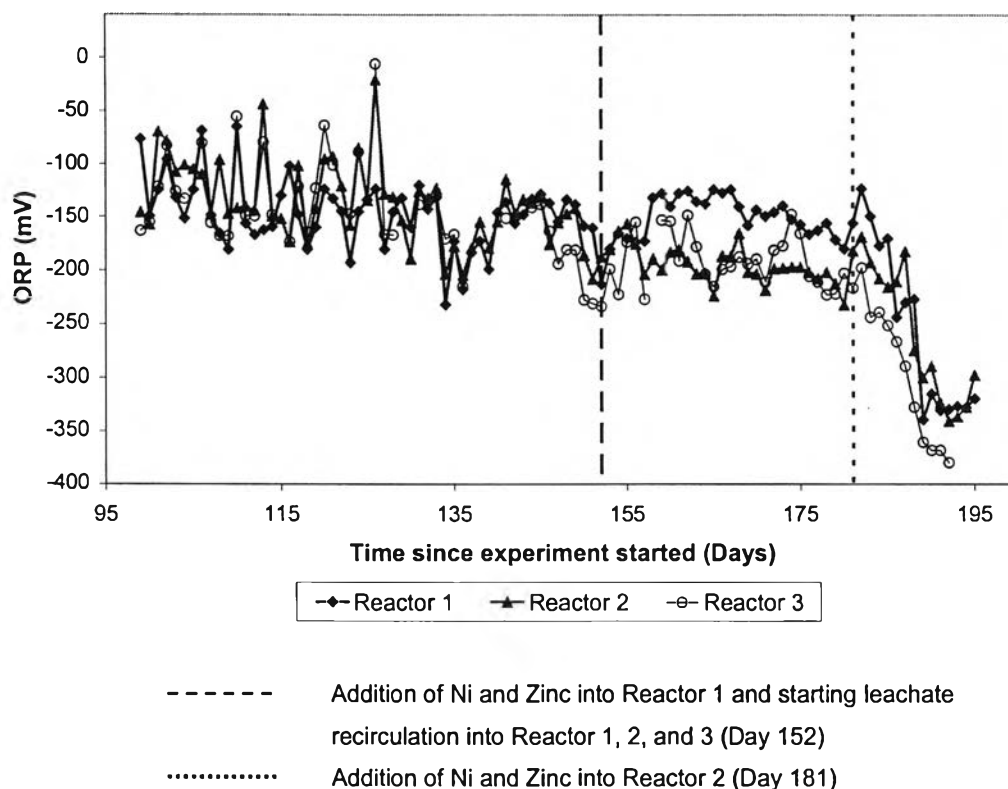


**Figure 4.3** Chemical Oxygen Demand of leachate from simulated landfill reactors.

#### 4.2.3 Oxidation-Reduction Potential

Oxidation-reduction potential (ORP) is a measure of the oxidation state of the system. Once the trapped air introduced with the refuse was depleted, the simulated landfill systems became anoxic, and proceeded to anaerobic. Then, the ORP became negative.

The leachate ORP measurement started on Day 99 because of lack of instrument in first period of experiment, as shown in Figure 4.4 (and Tables B-3 in Appendix B).



**Figure 4.4** Oxidation-Reduction Potential of leachate from simulated landfill reactors.

For reactor 1, reducing conditions were seen by Day 99 and ORP values decreased to -76.6 mV. Gradually decreasing of ORP value continued with an average about - 200 mV until the metal was added. After addition of metal on Day 152, ORP values were less negative indicating that the condition suitable for methanogenic was interrupted. The ORP values became more negative increased from Day 187 to Day 195 as waste stabilization proceeded, and was enhanced by leachate recycle.

For reactor 2, the ORP values were decreased from -145.8 mV on Day 99 to generally constant values of about -175 mV to Day 180 until the addition of heavy metals. After addition of metals on Day 181, ORP value was about -169.3 mV until Day 182. On Day 188 to 195, the ORP value was highly negative. The highly negative ORP were good for methanogenesis.

#### 4.2.4 Nutrients

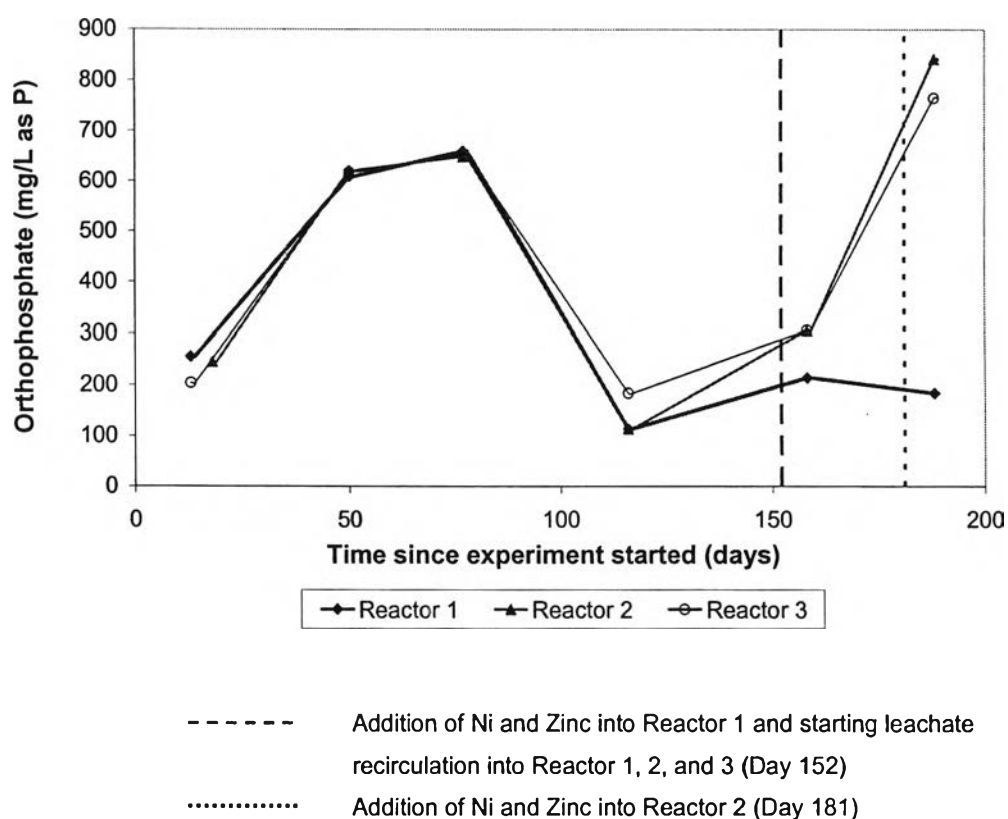
The availability of nutrients is essential to the microbially mediated processes of landfill stabilization. In order to ensure that adequate nutrients were available for biodegradation, orthophosphate and ammonia nitrogen concentrations were periodically measured as indicated in Figure 4.5 and 4.6 (Table B-4 and B-5 in Appendix B).

##### 4.2.4.1 Orthophosphate

The initial concentration of orthophosphate in three reactors (1, 2, and 3) was 255 mg/L, 204 mg/L and 847 mg/L respectively. However, orthophosphate concentrations began to decrease as a result of orthophosphate assimilation by microorganisms. The orthophosphate concentrations in all recycle reactors decreased on Day 77 to Day 116. This was attributed to microbial utilization, washout (dilution) and possible complexation reactions.

Leachate recirculation was established on Day 152, the orthophosphate concentration was continuously increased in reactors 2 and 3 on Day 152 to Day 195. This is directly associated with change in recycle rate from Day 152 to Day 195. On the other hand, reactor 1, after the addition of the metal salts, the orthophosphate concentration was slightly decreased on Day 152 to Day 195 as a result of precipitation with heavy metals. Similar observation was found on the study of Oney,(2003). The prevailing minimum concentration of 114 mg/L on Day 195 for Reactor 1 indicated sufficiency for biodegradation.





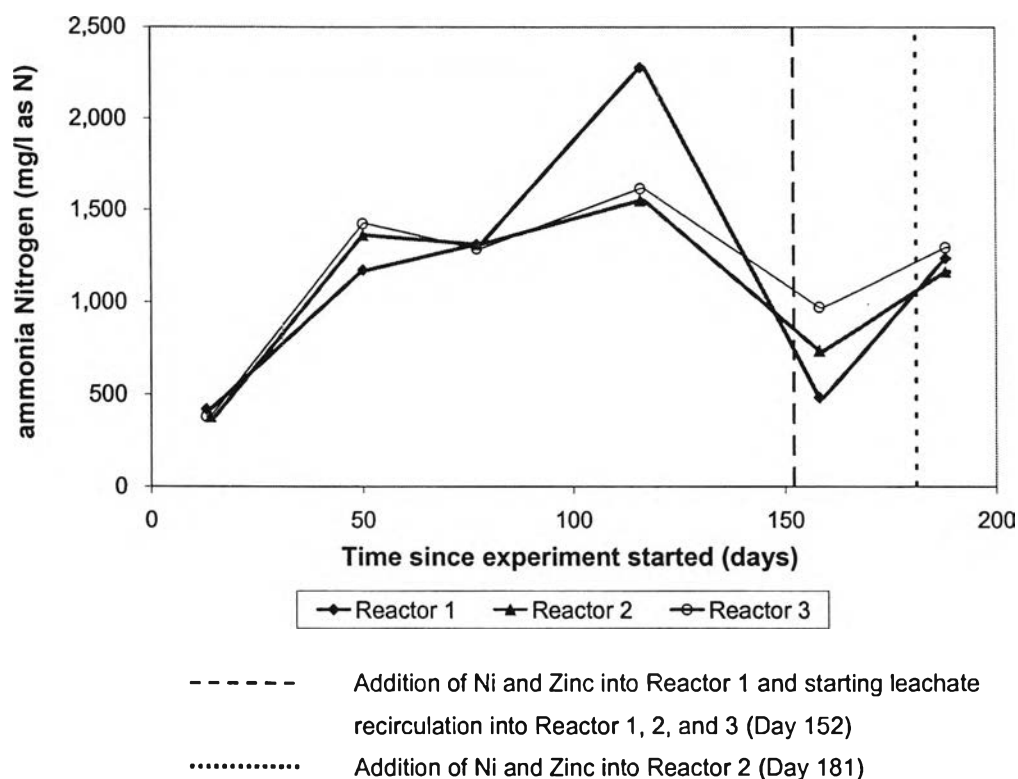
**Figure 4.5** Orthophosphate concentration of leachate from the simulated landfill reactors.

#### 4.2.4.2 Ammonia Nitrogen

The ammonia nitrogen in three simulated landfill reactors were found to be similar in concentrations, suggesting uniformity in nitrogen in refuse compositions for all reactors. Ammonia in the recycle reactors started to increase in response to the change in frequency of leachate recycle which promoted the release and containment of ammonia within the reactor.

After establishing relatively low initial concentrations, ammonia nitrogen ( $\text{NH}_3\text{-N}$ ) in all recycle reactors increased gradually between Day 13 to Day 50. The ammonia nitrogen was not dramatically different from Day 50 to Day 77. After that the ammonia nitrogen was increased on Day 77 to Day 116 and rapidly decreased on Day 116 to Day 158. On Day 152, the leachate recirculation was established in all

reactors, the ammonia nitrogen was increased on Day 158 to 188 due to accelerated leaching.



**Figure 4.6**  $\text{NH}_3\text{-N}$  concentration of leachate from the simulated landfill reactors

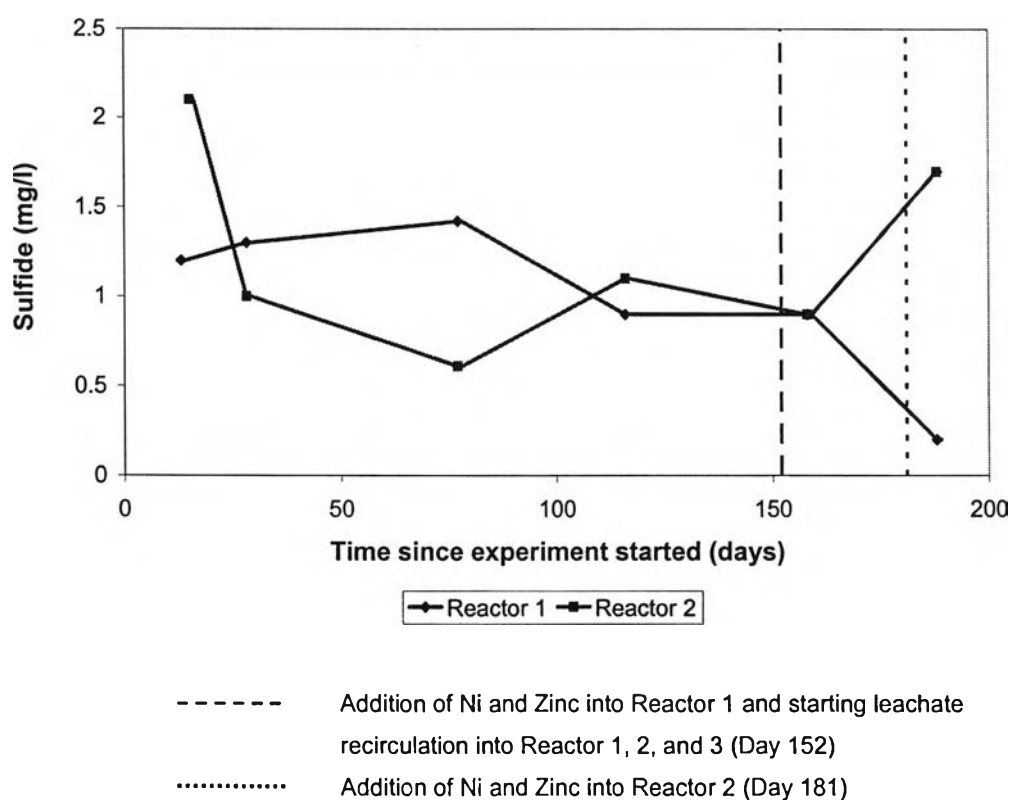
Measurement of ammonia was performed to assess nutrient availability in the three simulated landfill reactors. The results of analyses are expressed in mg/L of nitrogen and are presented in Figure 4.6, with corresponding data included in Table B-5 of Appendix B.

#### 4.2.5 Sulfides and Sulfates

Sulfides are another indicator of the presence of reducing conditions within the landfill environment. Sulfides are produced during anaerobic decomposition from the reduction of sulfates and other sulfur-containing inorganic compounds as well as from anaerobic protein degradation. In the  $\text{S}^{-2}$  form, sulfide is a powerful precipitating agent, even at low pH values and very low sulfide concentrations. Most of the sulfide

generated is bound to heavy metals as metal sulfides in anaerobic system (Pohland, 1993).

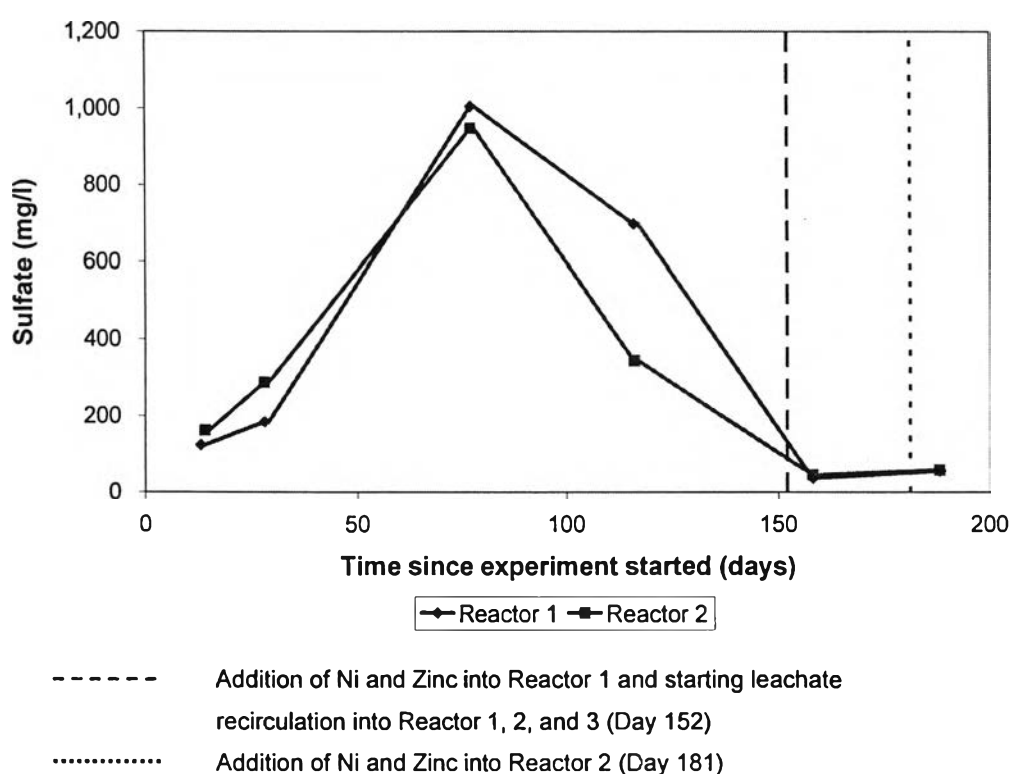
Since reducing conditions are particularly prevalent during later stages of landfill stabilization, sulfides were only periodically analyzed during the acid formation phase until the presence of sulfides was detected. The results of the sulfide and sulfate analysis are included in Figure 4.7 and 4.8, respectively (Table B-6 in Appendix B).



**Figure 4.7** Sulfide concentration of leachate from the simulated landfill reactors.

For reactor 1, all sulfur initially was in the form of sulfide because of the presence of the highly reducing environment in the reactors. Initial high sulfide concentration in the reactor was 1.2 mg/L on Day 13. However, starting on Day 14, sulfide concentrations in reactor 1 increased steadily until the maximum detected levels of 1.42 mg/L, were reached on Day 77. Subsequently, a gradually decline in

sulfide concentration in the reactor 1 was detected 0.2 mg/L on Day 188. As expected, sulfide concentration in this reactor was decreased from leachate by precipitation of heavy metals and product of hydrogen sulfide when organic sulfur compounds are decomposed by bacteria. On the other hand, the initial sulfate concentration was 124 mg/L on Day 13 and continuously increased on Day 28 to Day 77. After that, the sulfate concentrations were dramatically decreased on Day 78 to end of the experiment studied as a result of sulfates reduction to sulfides in Figure 4.8.



**Figure 4.8** Sulfate concentration of leachate from the simulated landfill reactors.

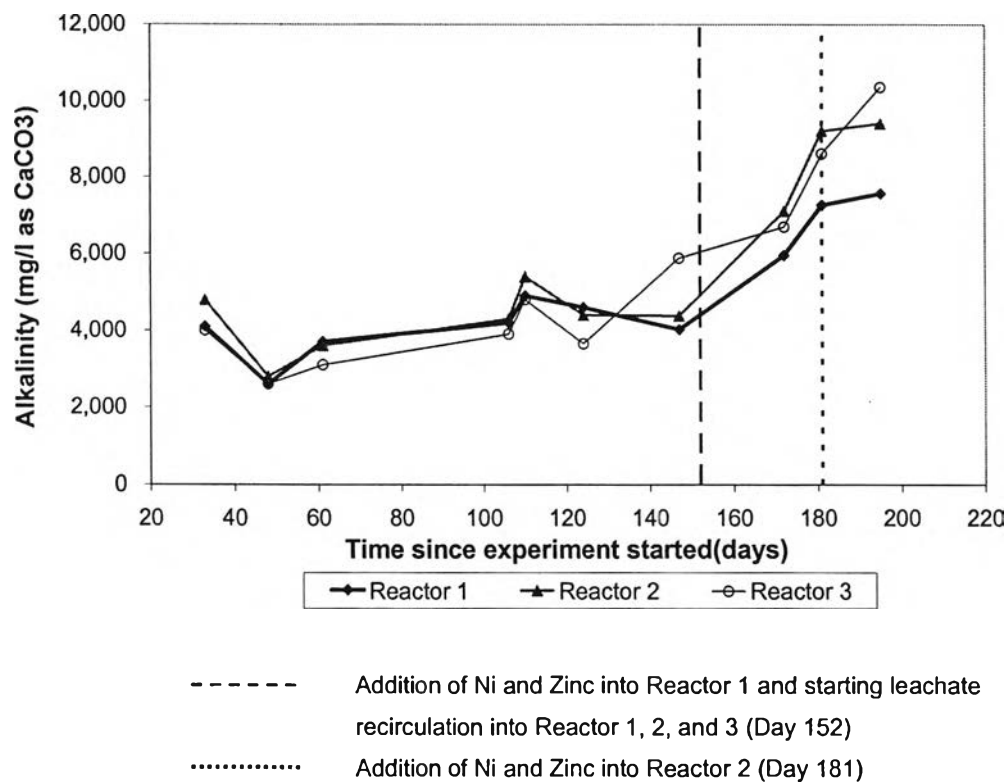
For reactor 2, initial sulfide concentration in the reactor was 2.1 mg/L on Day 13. A subsequent rapid decline in sulfide concentrations was also observed in the leachate from the reactor starting on Day 13 to Day 77. In addition, on Day 116, sulfide concentration was increased to about 1.1 mg/L. On Day 152, leachate recirculation was applied to this reactor. After addition of heavy metal on Day 181, sulfide concentration in this reactor was increased. There are many reasons to explain this point, may be an error from analytical value or the mixing was not yet completed.

The initial sulfate concentration was 162 mg/L on Day 13 and continuously increased on Day 13 to Day 77. Moreover, sulfate concentrations were dramatically decreased on Day 78 to Day 158. On Day 159 to Day 188, sulfates concentrations were not dramatically different from Day 158. Lower sulfate concentration occurred from sulfate reduction in this reactor.

#### 4.2.6 Alkalinity

For landfill leachate, total alkalinity measurement reflects the relative presence of acids and bases such as  $\text{H}_2\text{CO}_3$ ,  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$ , TVA, phosphorus and ammonia. The total alkalinity of leachate during the acid formation phase is dominated by the volatile organic acids and the associated buffer system due to the high concentrations present and the fact that they are stronger acids than those constituting the bicarbonate buffer system. The total alkalinity concentrations are presented in Figure 4.8 (Table B-7 in Appendix B).

The initial alkalinity values in three reactors were 4,100 mg/L as  $\text{CaCO}_3$ , 4,800 mg/L as  $\text{CaCO}_3$  and 4,000 mg/L as  $\text{CaCO}_3$ , respectively. The total alkalinity of all three simulated landfill reactors was steadily increased from 2,600 mg/L as  $\text{CaCO}_3$  on Day 48 to 4,900 mg/L as  $\text{CaCO}_3$  on Day 110 in Reactor 1, 2,800 mg/L as  $\text{CaCO}_3$  on Day 48 to 54,000 mg/L as  $\text{CaCO}_3$  on Day 110 in Reactor 2 and 2,600 mg/L as  $\text{CaCO}_3$  on Day 48 to 48,000 mg/L as  $\text{CaCO}_3$  on Day 110 in Reactor 3, respectively. However, the alkalinity was not dramatically different from Day 111 to Day 147. After that on Day 152 to Day 195, was applied leachate recirculation in this recycle reactor. With the addition of NaOH buffer solution for pH adjustment purposes, the pH values rose from 5.60, 5.43 and 5.63 to 7.10, 7.03, and 7.10 respectively from Day 172 to Day 195 and alkalinity increased to 7,560 mg/L as  $\text{CaCO}_3$ , 9,400 mg/L as  $\text{CaCO}_3$ , and 10,350 mg/L as  $\text{CaCO}_3$  on Day 195.



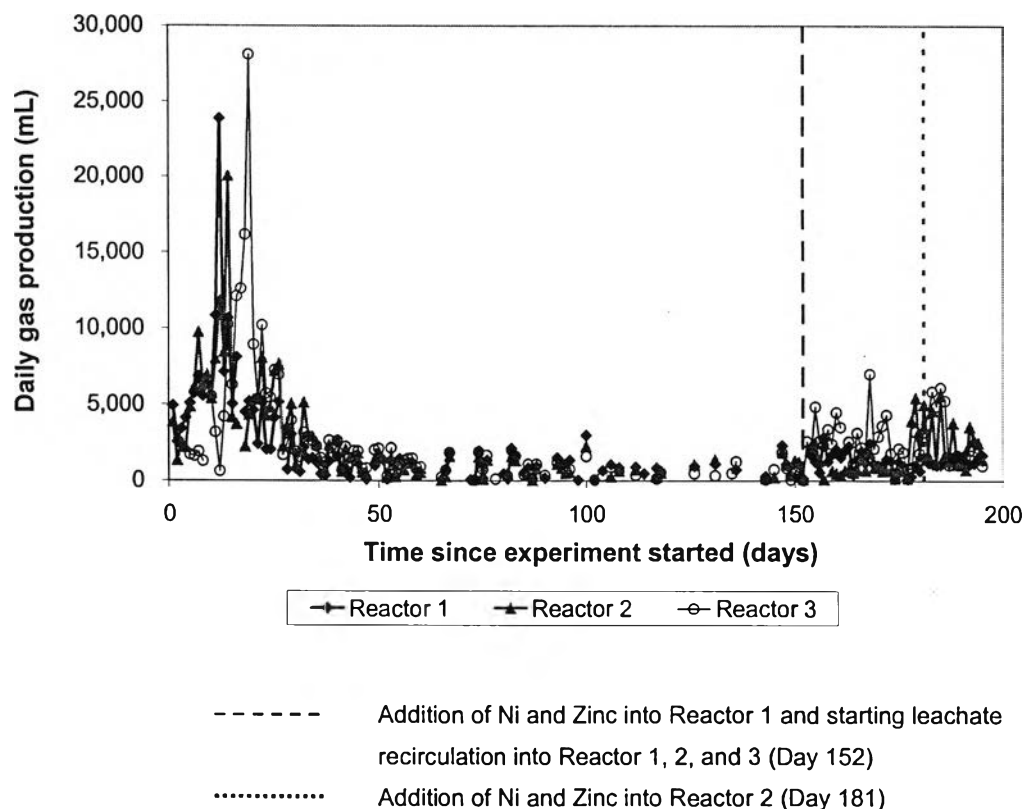
**Figure 4.8** Alkalinity of leachate from the simulated landfill reactors.

### 4.3 Gas Analysis

Gas volume and gas composition from three simulated landfill reactors were monitored as the main indicators of the progression of solid waste stabilization processes and as an indicator of the rate of biological activity and organic material conversion within the landfill environment.

#### 4.3.1 Gas Production

Daily gas volumes produced for three reactors are shown in Figure 4.9 (Table C-1 in Appendix C). Cumulative gas volumes produced in the all reactors are presented in Figure 4.10 (Table C-2 in Appendix C).



**Figure 4.9** Daily gas Production of the simulated landfill reactors.

Some gas production began immediately after moisture addition to the cells and leachate production began on Day 0. The initial gas production rate in Reactors 1, 2, and 3 were 4,915 ml, 3,850 ml, and 1,700 ml, respectively. The daily gas volumes were continuously decreased on Day 51 to Day 141.

After addition of sludge seeding on Day 142, the gas productions were continuously increased in all reactors. For reactor 1, after addition of heavy metal on Day 152, gas production rate was not greater than 2 L per day until Day 195. The low volume of landfill gas generated in this reactors was directly associated with the continuity of biological activity even in the presence of heavy metals.

For reactor 2, after establishing leachate recirculation on Day 152, gas production rate was slightly increased until Day 165. After increasing leachate

recirculation ratio on Day 166, gas production rate was continuously increased. Large volumes of gas production were often observed on the days following leachate recycle. However, on Day 179, methane fermentation phase was established in this reactor, gas production rate for the recycle reactor increased dramatically during Day 179 to Day 192. Furthermore, increases in leachate recirculation frequency had proven to directly impact the gas generation potential. Increased gas production was directly related to the higher degree of stabilization in the recycle reactor and may be attributed to the leachate recirculation scheme employed. Buffering of leachate prior to its recirculation during this phase resulted in establishing environmental conditions favored by methanogens which accelerated waste degradation and resulted in a further increase of gas production that reached its peak during this phase

For reactor 3, after applying leachate recirculation on Day 152, gas production rate was increased because liquid, which was a substrate distributing medium, became more uniformly distributed and more available for microbial utilization after recirculation. The overall volume of gas produced was much larger in the reactor 3 than in the reactors 1 and 2.

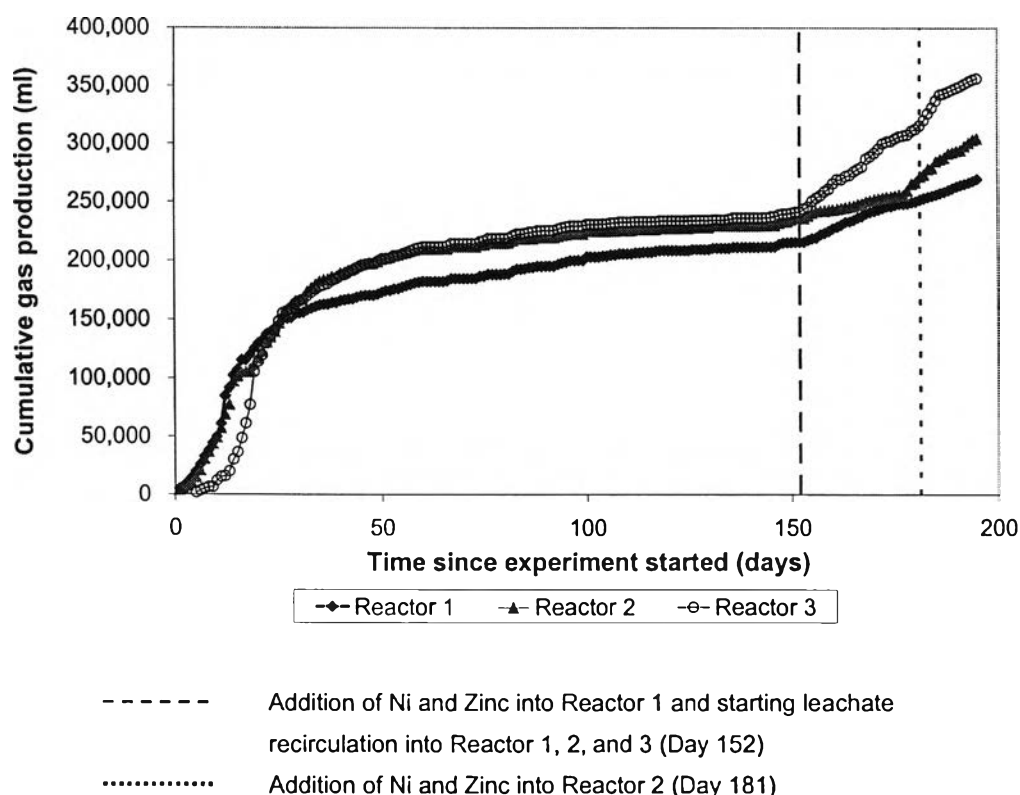
For daily gas production parameter and cumulative gas production, it was not obvious indicator for evidence of impact of nickel and zinc in this experiment. In addition, it was found that room temperature has affected on daily gas production. After leachate recycle started, high value gas production were found in all reactors and initial amount of gas production was lower in reactor 1 as shown in Figure 4.10.

However, for this experiment, the cumulative gas methane production was an obvious indicator for evident of impact of nickel and zinc on degradation of organic waste in landfill reactor. The cumulative gas methane production was presented in Figure 4.11 (Table C-3 in Appendix C).

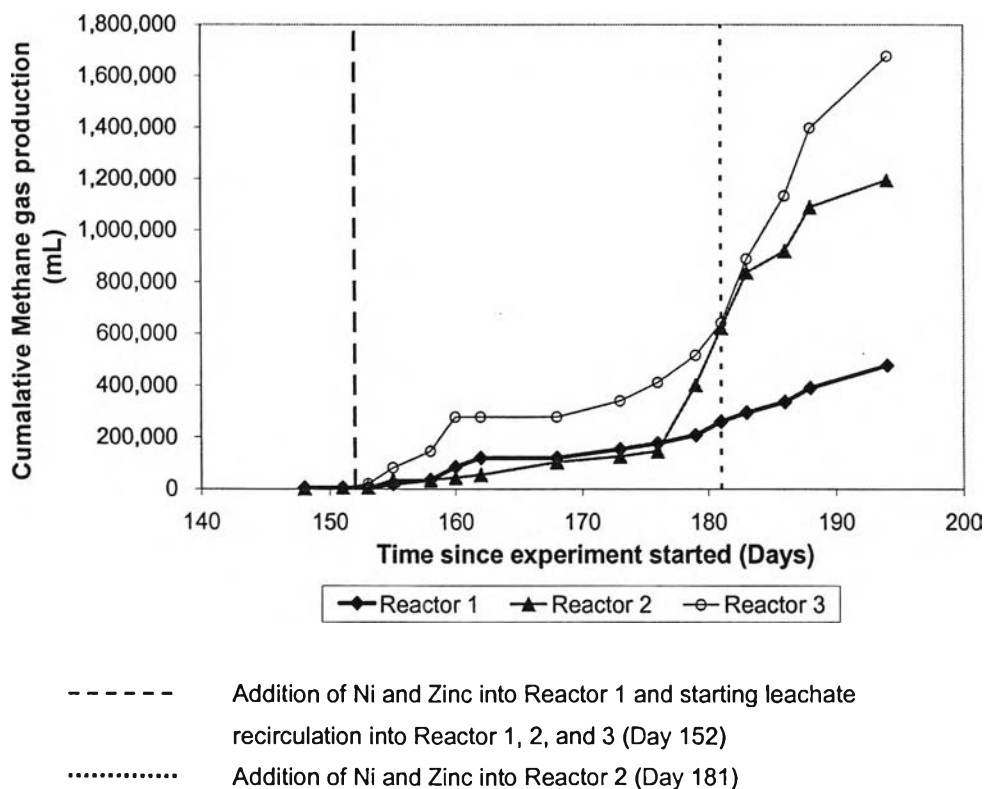
The data of cumulative methane production were available since Day 148 due to the availability of instrument (GC-TCD). For reactor 1, from Figure 4.11, it can be seen that after addition of heavy metals on Day 152, daily gas production rate and



cumulative methane production were lower than reactors 2 and 3. Moreover, the cumulative methane production was constant until the end of experiment confirming the methanogenic populations within the reactors were inhibited by the presence of heavy metals. For reactor 2, after addition of heavy metals on Day 181, the cumulative methane production continued in this reactor without any obvious heavy metals inhibition. After the onset of methane fermentation on Day 179, the cumulative methane gas was dramatically increased until Day 195 indicated an established methanogenic activity. Further increases in the leachate recirculation ratio resulted in high methane concentrations. The increase in recirculation ratio had a positive effect on methanogenic population, enhancing their growth and activity due to the increase in moisture content. For reactor 3, the cumulative methane production was continuously increased until the end of experiment studied and the cumulative methane production reached its highest value of approximately 1,676.50 L.



**Figure 4.10** Cumulative Gas Production of the simulated landfill reactors.



**Figure 4.11** Cumulative Methane Production of the simulated landfill reactors.

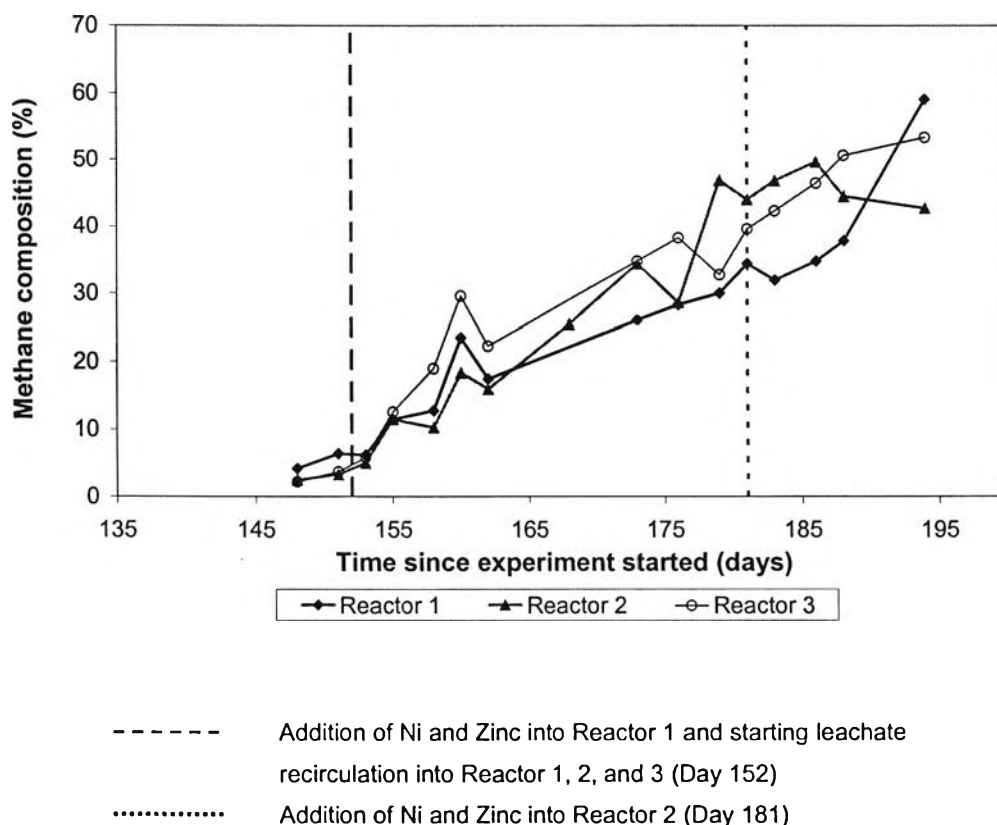
### 4.3.2 Methane Production

For this experiment studied methane percentages as indicator for changing leachate recirculation ratio and changing of phase in landfill stabilization. Methane percentages for three simulated landfill reactor are presented in Figure 4.12 (Table C-4 in Appendix C).

The data of methane percentage were available since Day 148 due to the availability of instrument. On day 148 to 153, methane percentages were low because of leak of some parts of reactors. After reactors were renovated, the methane percentages were dramatically increased in all reactors. As expected, the system was completed.

In three simulated landfill reactors, the methane fermentation phase was started when the initial methane concentration was approximately 40%. For reactor 1, after the onset of methanogenic condition on Day 193, the methane concentration reached 59.03% at the end of the experiment. On the other hand, in the reactor 2, the initial methane concentration of 46.88% on Day 179 was observed due to the established methanogenic conditions. Methane production decreased to 42.66% at the end of the study due to washout of organic carbon from the system. For reactor 3, a high initial methane concentration of 42.29% was observed due to the established methanogenic conditions on Day 183. Methane production increased to 53.29 % at the end of the study.

The following can be concluded that, reactor 1 had slower stabilization, thereby extending the acid formation and methane fermentation phases of waste stabilization and lower methane gas production rate.



**Figure 4.12** Methane Percentage of the simulated landfill reactors.

#### 4.4 Leachate Recirculation

This system is designed to distribute recirculated leachate uniformly throughout the all simulated landfill reactors. The volume of moisture present in each reactor was essential with regards to the anaerobic systems and leaching of heavy metals studied. Data and computation for moisture available until Day 195, which the end of experiment studied, are presented in Table E-1-E-2 of Appendix E.

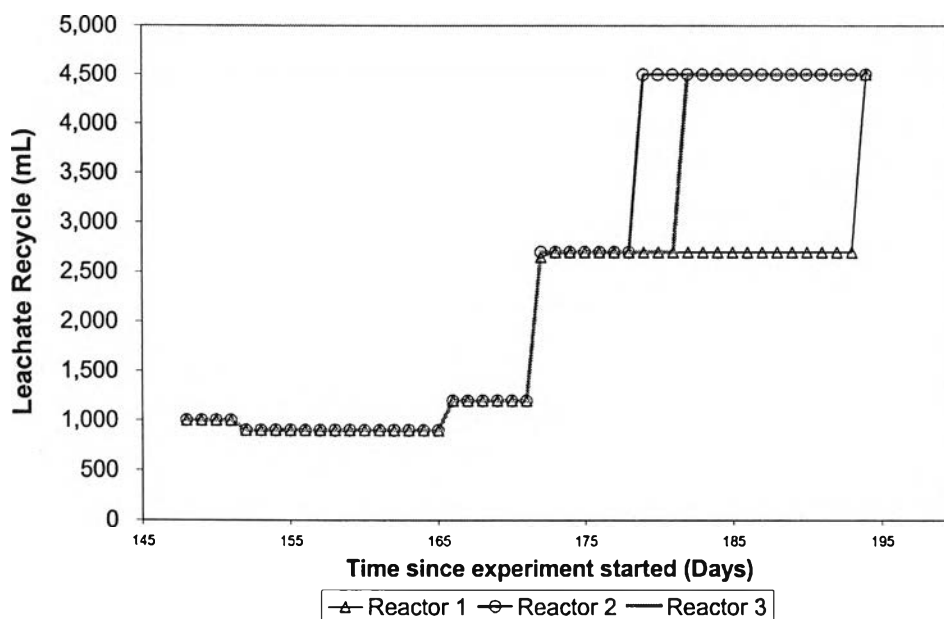
Computations for the moisture present were based on volume of liquid originally present, the introduced liquid, and the liquid lost from the systems. The recycle reactor 1, 2, and 3 initially contained 17.96, 18.29, and 18.54 liters of liquid at Day 0, respectively. The introduced liquid volumes were buffer solutions, sludge seeding for the recycle reactor, and metal salts added to the both reactors. The liquid loss was primarily due to sampling for the recycle reactor. Evaporation in this case was not an important factor contributing to water loss, since the reactors were operated at room temperature (Austin, 1984).

After 195 days of operation, the recycle reactor 1 was found to hold a total of about 21.31 liters in the reactor, while the reactor 2 held 21.58 liters of moisture in the reactor and 22.29 liters in reactor 3.

The leachate recirculation ratio of this experiment studied was basically divided in to five stages depending on amount of methane percentages. The volume of leachate recycles for all reactors are presented in Figure 4.13. However, actual stages observed in stabilization were classified into two types: acidogenesis and methanogenesis.

For reactor 1, the onset of acidogenic formation began on Day 152. The reactor was using everyday recirculation of 900 mL leachate with a buffer solution of 5 N NaOH on Day 152 to Day 165. The recirculation ratio was readjusted to 1,200 mL and 2,700 mL on Day 166 to Day 172, and Day 173 to Day 193, respectively. In the second period, the onset of methanogenic conditions on Day 194 was operated using

everyday recirculation of 4,500 mL leachate for one day at the end of the study. Leachate recycle volume for this reactor was kept at 2,700 ml/day during Day 173 to Day 193 due to the fact that percent methane was lower than forty, as indicator of changing in state. This may be due to inhibition from nickel and zinc addition on Day 152.



**Figure 4.13** Leachate Recirculation Applications on Day 152 to Day 195 in Reactor 1, 2, and 3

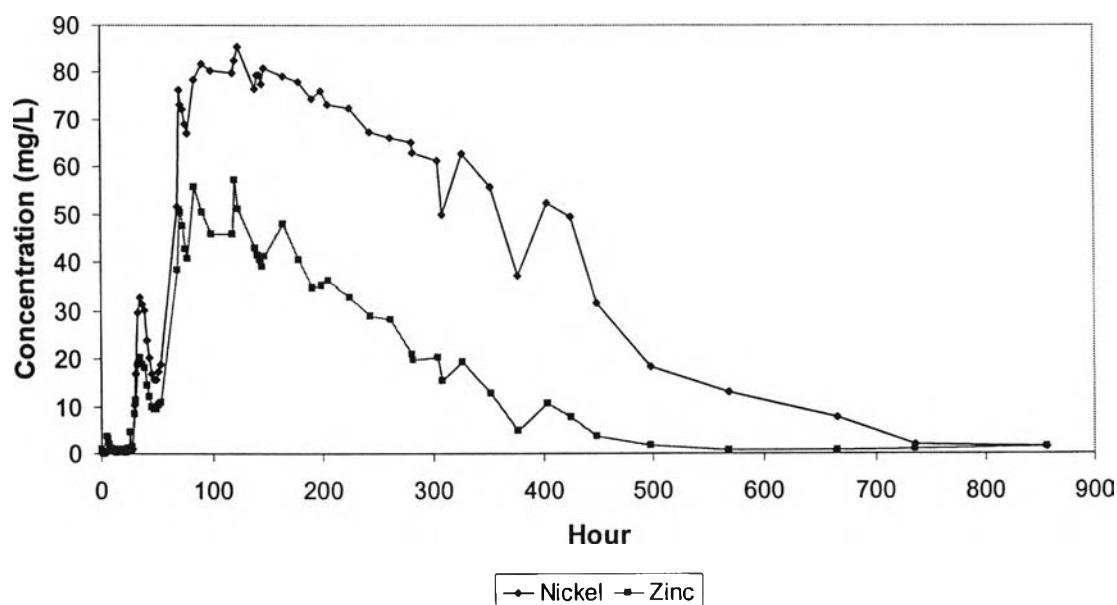
For reactor 2, was divided into two periods. In the first period, the onset of acidogenic formation on Day 152, the reactor was using everyday recirculation of 0.9 L leachate with a buffer solution of 5 N NaOH on Day 152 to Day 165. The recirculation ratio was readjusted to 1,200 mL and 2,700 mL on Day 166 to Day 171, and Day 172 to Day 178, respectively. In the second period, the onset of methanogenic conditions on Day 181 was operated using everyday recirculation of 4,500 mL leachate starting on Day 179 until the end of the study.

For reactor 3, was divided into two periods. In the first period, the onset of acidogenic formation on Day 152, the reactor was using everyday recirculation of

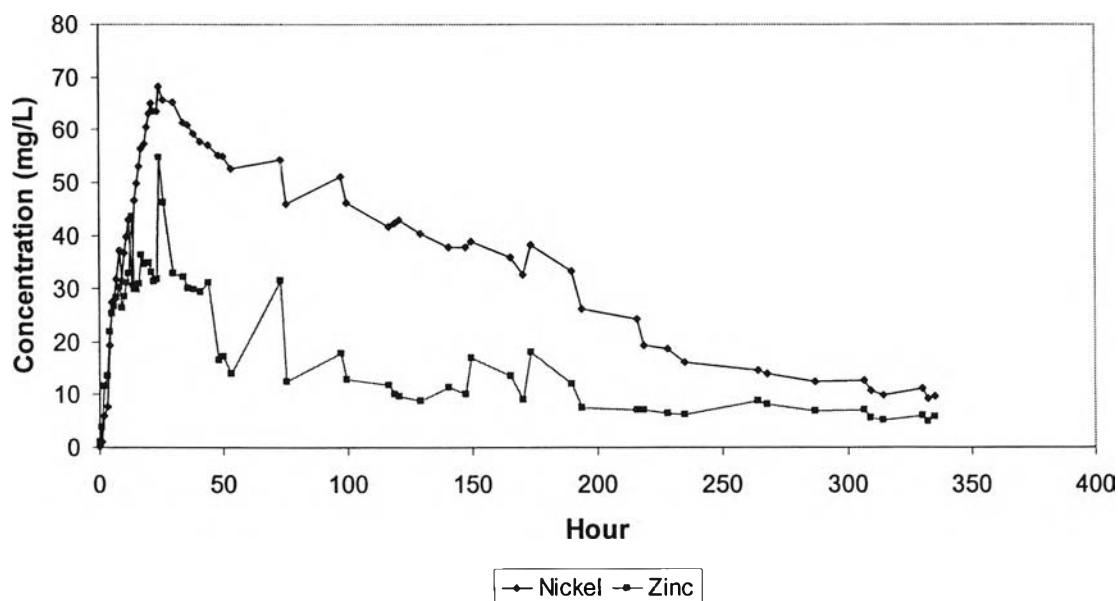
methanogenic conditions on Day 183 was operated using everyday recirculation of 4,500 mL leachate until the end of the study.

#### 4.5 Heavy Metals Analysis

Heavy metals were analyzed during experimental investigations: nickel and zinc. The most important factor in determining the presence of a metal in leachate is its solubility under the conditions prevailing within the landfill environment. Several factors influence metal solubility in leachate, including concentration of precipitant species (hydroxides, carbonate, and sulfide), presence of complexing agents (ligands), ORP, pH, ionic strength and washout effects.



**Figure 4.14** Nickel and zinc during acidogenic phase (On day 152 to day 195).



**Figure 4.15** Nickel and zinc during methanogenic phase (On day 181 to day 195).

#### **Reactor 1: Nickel and zinc added during Acidogenic Phase**

During Acidogenic Formation phase, it was established on Day 152, nickel and zinc were loaded into this reactor according to the amounts suggestion for co-disposal under the directives of Turkish Hazardous Waste Control Regulations. The influent concentrations of nickel and zinc loaded into this reactor about 87.90 mg/L. They were monitored for 44 days. The effluent concentrations of nickel and zinc during acidogenic phase were shown in Figure 4.14 (see attached data in Table F-1, Appendix F). The first period, from beginning to hour 26, no significant concentration levels of nickel and zinc were found in the effluents. Between hour 26 and hour 51, there was a small peak of heavy metal concentrations from the leakage of heavy metals in reactors. After that the effluent concentration of both heavy metals was dramatically increased. The effluent concentration was increased as a result of mobilization and complexation was found to be the principle mechanisms for increasing concentrations of heavy metal species in the leachate. Consequently, at approximate range of hour 70 to hour 124, it can be noted that nickel and zinc reached

Concentrations at peak time of nickel and zinc were about 85.3 mg/L at hour 124 and 55.75 mg/L at hour 84, respectively. The metals were believed to be precipitated as immobile sulfides and adsorbed onto waste particles. Therefore, the concentration of both nickel and zinc was slightly and continuously dropped until the end of monitoring period. A retention time of heavy metal in reactor can be defined as an average time of soluble metals remaining in leachate from the recycle reactor. In this work, it was found that the retention times of nickel and zinc were 179 hours and 140 hours, respectively. Heavy metal retention time for nickel and zinc in the recycle reactors was computed according to this following equation (1);

$$T_R = \frac{\sum(C_i * T_i)}{\sum C_i} \dots \dots \dots (1)$$

$T_R$  = Retention time, hours

$C_i$  = Heavy metals concentration, mg/L

$T_i$  = time when heavy metals concentration  $C_i$  was observed, hours

**Reactor 2: Nickel and zinc added during methanogenic fermentation.**

Similar results were observed in reactor 2. During methanogenic fermentation phase starting on Day 181, influent concentration of nickel and zinc was loaded into this reactor about 92.70 mg/L. Nickel and zinc were monitored for 15 days. The effluent concentrations of nickel and zinc during methanogenic phase were shown in Figure 4.15 (see attached data in Table F-1, Appendix F). From the beginning, concentration levels of nickel and zinc were continuously increased until breakthrough at hour 21 and hour 17, respectively. As mentioned above, there were no additional heavy metals put into the reactor; therefore, the concentrations of both heavy metals were dropped. Moreover, the major mechanism for decreasing of both heavy metals in the effluents was precipitation and complexation with sulfide and carbonate anions (Pohland, 1986). Effluent concentration of nickel was higher than zinc. Because of during methanogenic formation in this reactor, the range of pH was between 6.4 and 7.03. Consequently, zinc can be precipitated with a variety of anions



including sulfide, phosphate, carbonate, and silicate (Stumm and Morgan, 1970; Fuller, 1977). Metal concentrations tend to be limited by carbonate and sulfide solubility in anaerobic system. Metal solubility generally decreases as pH rises in the range of 5 to 9 (Rushbrook, 1988).

Concentrations at peak time of nickel and zinc were about 64.9 mg/L at hour 21 and 36.2 mg/L at hour 17, respectively. The retention times of nickel and zinc in reactor were 71 and 57 hours, respectively.

From the results obtained in Reactor 1 and 2, heavy metal retention times and heavy metal effluent concentrations were compared. The reactor 1 had longer retention time than reactor 2. This meant that heavy metals could be stayed in liquid phase for longer time and remained toxic to microbial community in the reactor 1, this also supported by amount of metal precipitations in the reactor during that period of time. However, concentration tended to decrease as a result of soluble metals precipitate as insoluble sulfides, carbonates, hydroxides and possibly phosphates in landfills (Pohland, 1991). Moreover, there are many mechanisms of zinc and nickel removal in landfill. The major attenuation mechanisms for zinc are adsorption, cation exchange, and precipitation. Zinc is a common cation in soil systems. As is true with other cations, the pH of the leachate- soil system is crucial factor in zinc removal, reflecting the influence of dominant hydrolysis species on both the affinity for soil colloids and the solubility of zinc (Gebhard, 1978). The attenuation of zinc was found to increase rapidly for a pH change from 2 to 8 with a significant rise around 6 to 8 (Griffin et al., 1976). The major attenuation mechanism of nickel includes sorption and precipitation. In addition, the result showed that the time period of heavy metal remaining in solution of reactor 2 might be shorter. This was due to the condition in reactor 2 that was favorable for soluble metals precipitation.