EVALUATION OF *IN SITU* LEACHATE MANAGEMENT ALTERNATIVES ON MUNICIPAL SOLID WASTE STABILIZATION IN SANITARY LANDFILLS

by

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B.S. in Environmental Engineering, Marmara University, 1997

Submitted to the Institute of Environmental Sciences in partial fulfillment of the
requirements for the degree of
Master of Sciences
in
Environmental Technology

Boğaziçi University
1999

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ACKNOWLEDGMENTS

I would like to express my sincere gratitude to **Assis. Prof. Dr. Turgut T. Onay** for his great deal of interest, scientific guidance, and encouragement throughout this study.

I wish to extend my thanks to my friend and fellow graduate student **Başak Güleç** for her friendship and help during the laboratory work.

I am most thankful to the academic stuff of the Institute of Environmental Sciences at Boğaziçi University, for their generous assistance during the study period.

I would like to acknowledge with thanks **Boğaziçi University Research Fund** for financing this project.

I would like to acknowledge with appreciation **İZAYDAŞ** for their generous help at the beginning of the study.

I wish to express my deepest thanks to **Fethi Silajdžić** who belived in me and was always there when I needed him most.

Finally, I would like to dedicate this work to my parents **Nihad and Maida Šan,** and my brother **Taner Šan,** because they were always by my side with their patience, tremendous support, and constant encouragement.

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Master of Science in Environmental Technology, 1999

Advisor: Assis. Prof. Dr. Turgut T. Onay

Keywords: leachate recirculation, landfill stabilization

An alternative approach for treating municipal solid waste involves the treatment of the waste after landfilling by addition of moisture to the waste. Increasing attention is being given to municipal solid waste landfill leachate recycle (recirculation) as a means of *in situ* leachate treatment and landfill stabilization. Using a leachate recycle, a landfill may be operated as a municipal solid waste bioreactor treatment system rather than as a conventional waste dumping site.

In order to study the feasibility of an *in situ* leachate management alternative to provide leachate treatment and waste stabilization two landfill simulating reactors, one with leachate recycle and one without, were constructed and sited in the laboratory's hot room (34°C). Leachate recirculation volume and frequency of recirculation were changed periodically to investigate the effects of different operational moisture regimes on waste stabilization and leachate treatment. Both reactors were filled with municipal solid waste having typical solid waste composition determined in Istanbul.

This research showed that the leachate recirculation is a feasible way to treat the leachate *in situ*, and, therefore, decrease the cost of further external treatment. Leachate recirculation management strategy accelerates the stabilization rate of waste matrix, decreasing time required for stabilization to a matter of months rather than years. Four times per week recirculation strategy was found to provide highest degree of waste stabilization.

DÜZENLİ DEPOLAMA SAHALARINDA OLUŞAN SIZINTI SULARININ DAHİLİ ARITIM ALTERNATİFLERİNİN DEĞERLENDİRİLMESİ

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Anahtar sözcükler: sızıntı suyunun geriye devri, depolama sahasının stabilizasyonu

Katı atıkların arıtılmasında alternatif yöntem, depolamadan sonra atıkların nem oranını artırmaktır. Sızıntı suyunun geriye devri sonucunda, sahada sızıntı suyunun arıtılması ve depolama sahasının hızlandırılmış stabilizasyonu sağlanır. Sızıntı suyu geri devireltirirek, düzenli depolama sahası katı atık bioreaktör arıtma sistemine dönüşmektedir.

Sahada katı atık ve sızıntı sularının arıtılmasına neden olan, sızıntı suyunun geriye devri yöntemini değerlendirmek amacıyla, 34°C sabit sıcaklıkta, geri devirli, ve diğeri, geri devirsiz, iki reaktör kullanılmıştır. Değişik olarak uygulanan nem rejimlerinin, katı atık stabilizasyonu ve sızıntı sularının arıtılmasındaki etkilerini incelemek için, sızıntı suyunun geriye devir hacmı ve sıklığı zamana bağlı olarak değiştirilmiştir. İki reaktörde de, İstanbul şehrinde kompozisyonu belirli, katı atıklar kulanılmıştır.

Bu araştırma, sızıntı suyunun geriye devir yönteminin, sahada sızıntı suyunun arıtılmasında uygunluğunu göstermektedir, ve bu nedenle de, müteakip harici arıtmanın maliyetini düşürmektedir. Sızıntı suyunun geriye devri kullanım yöntemi katı atık stabilizasyonunun oranını hızlandırmaktadır. Depolama sahalarının stabilizasyon süresi yıllar değil, aylarla sınırlı olacaktır. Haftada dört kez geriye devir stratejisi, atık stabilizasyonunun azami derecesini temin etmek amacıyla uygun bulunmuştur.

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1. INTRODUCTION

Solid waste is generated as a consequence of a variety of social activities. Problems associated with solid waste disposal in the early times were less pronounced than today due to a smaller generator population, less technological advances, and larger areas available for assimilation of wastes.

In Istanbul, the solid waste issue presents one of the main environmental questions. The amount of solid waste generated increases rapidly as a result of population increase and technological development. If assumed that the population in Istanbul will reach 17 millions by the year 2020, the amount of solid waste generated would increase by 25%, which means an increase from 0.63 kg/capita.d in the year 1990, to 0.8 kg/capita.d in the year 2020. Of the total waste generated, a small fraction is recycled, composted, or incinerated, and the unprocessed part is sent to two sanitary waste disposal sites. Theoretical amount of leachate produced at the landfill sites in Istanbul is $2m^3$/ha.day for first five year after encapsulation, and $5m^3$/ha.day for succeeding years [1]. The high volumes of leachate produced can pose a threat to the environment if not managed properly. Therefore, it is very important to find out the ways to treat leachate, effectively and economically.

Although sanitary landfilling is the cheapest method of solid waste disposal, there are several disadvantages that must be considered. Besides leachate and gas production, one of the important disadvantages represents the slow rate of waste degradation and stabilization which may delay the future use of the disposal site for long period of time. Operating the landfill as a "dry tomb" [2], by diverting all moisture except direct precipitation, minimize leachate production. However, it also reduces the rate of stabilization limiting the moisture and necessary nutrient transport, therefore limiting the rate of biological activity in the landfill. Period required for landfill stabilization prolong, allowing high organic content to remain in the leachate for long period of time and exposing surface and groundwater to highly contaminated leachate for several years. Furthermore, insufficient moisture will create dry condition in the landfill, making compaction necessary and difficult, creating extra expenditure [3].

The technique of operating landfill under wet conditions to accelerate the decomposition of the landfilled waste offers an alternative management approach. Using a technique known as leachate recycle (recirculation), a landfill may be operated as a municipal solid waste bioreactor treatment system rather then as a conventional waste dumping site.

The objective of this research was to develop and study the feasibility of a *in situ* leachate management alternative to provide leachate treatment and waste stabilization. Furthermore, leachate recirculation volume and frequency of recirculation were changed periodically to investigate the effects of different operational moisture regimes on waste stabilization and leachate treatment. For this purpose, two landfill simulating reactors, one with leachate recycle and one without, were constructed in the laboratory. Both reactors were filled with shredded and compacted municipal solid waste having typical solid waste composition determined in Istanbul. Reactors are sited in the constant temperature hot room (34°C) to enhance the growth of anaerobic microorganisms. Making certain modification, such as, introducing a leachate collection system, leachate recirculation, and gas collection system, landfill simulating reactors were converted into controlled anaerobic bioreactors.

The results obtained from two reactors were compared to evaluate the effect of leachate recycle as an leachate management option. Furthermore, the optimum volume of leachate to be recirculated and frequency of leachate recirculation were determined. The results and conclusion from this study are going to be submitted to the Istanbul Municipality to offer an alternative solution to leachate management.

2. LITERATURE REVIEW

Landfills are the physical facilities used for the disposal of residual solid wastes in the surface soils of the earth. Landfills can be classified into three categories. "Sanitary landfill" term is used to describe the landfills as an engineering facility for the disposal of municipal solid waste designed and operated to minimize public health and environmental impacts. Hazardous wastes are disposed in the "secure landfills". The "controlled landfills" are designed and operated to provide attenuation of both nonhazardous and hazardous constituents that may be codisposed with the municipal solid waste as a result of residential, commercial, and industrial activities [4].

Until 1953, solid wastes generated in Istanbul were disposed into the sea. Discovery of potential waste disposal areas resulted in the substitution of sea disposal with open dump disposal [5]. Except the two sanitary landfills constructed in the last few years, a high percentage of the municipal solid waste generated in the Istanbul is still disposed in the open dumps.

2.1. Landfill Stabilization

2.1.1. Microbiology of Landfill Stabilization

A solid waste landfill can be conceptualized as a biochemical reactor, with solid waste and water as the major inputs and with landfill gas and leachate as the principal outputs. Leachate and gas are produced as a result of many biological, chemical and physical reactions including: (1) biological decomposition of degradable material by either aerobic or anaerobic processes with gas production; (2) biochemical oxidation of organic and inorganic portions in the solid waste; (3) diffusion and transport of gases; (4) dissolution and transport of constituents by leaching; (5) sorption on waste matrix; (6) liquid hydraulic transport; (7) movement of dissolved constituents as a result of concentration gradient; and, (8) differential settlement of landfill layers resulting from waste degradation and consolidation of material into void spaces [6]. Waste decomposition process in landfills proceed under anaerobic conditions, therefore, the fundamentals and principles of anaerobic treatment are applicable to the landfills as well. The metabolic stages involved in the anaerobic decomposition of the solid waste are hydrolysis, acidogenesis, acetogenesis, and methanogenesis.

In the first two stage solid and complex, dissolved organic compounds are hydrolyzed and fermented to primarily volatile fatty acids, alcohols, hydrogen, and carbon dioxide. In the second stage, an acetogenic group of bacteria converts the products from the first stage to acetic acid, hydrogen, and carbon dioxide. In the final stage, methane is produced by the methanogenic bacteria. This may be done by hydrogenophilic bacteria converting hydrogen and carbon dioxide to methane [7]. The overall process including major bacterial groups and substrates is illustrated in the Figure 2.1. The key microbial groups involved in municipal solid waste stabilization and the substrates they are feed on are given in Table 2.1.

Table 2.1. Key Physiological Groups of Microbes Involved in Anaerobic Degradation Process [8]

MICROBIAL GROUPS	CHEMICAL SUBSTRATES
Amylolytic bacteria	Starches
Proteolytic bacteria	Proteins
Cellulolytic bacteria	Cellulose
Hemicellulolytic bacteria	Hemicellulose
Hydrogen-oxidizing methanogenic bacteria	Hydrogen
Acetoclastic methanogenic bacteria	Acetic acid
Sulphate-reducing bacteria	Sulphate

The hydrolysis process initiate the decomposition of the solid waste by reducing complex organic matter to smaller soluble components by means of extracellular enzymes produced by fermenting bacteria [9]. There is disagreement between authors about hydrolysis being the rate limiting step of anaerobic conversion of solid waste.

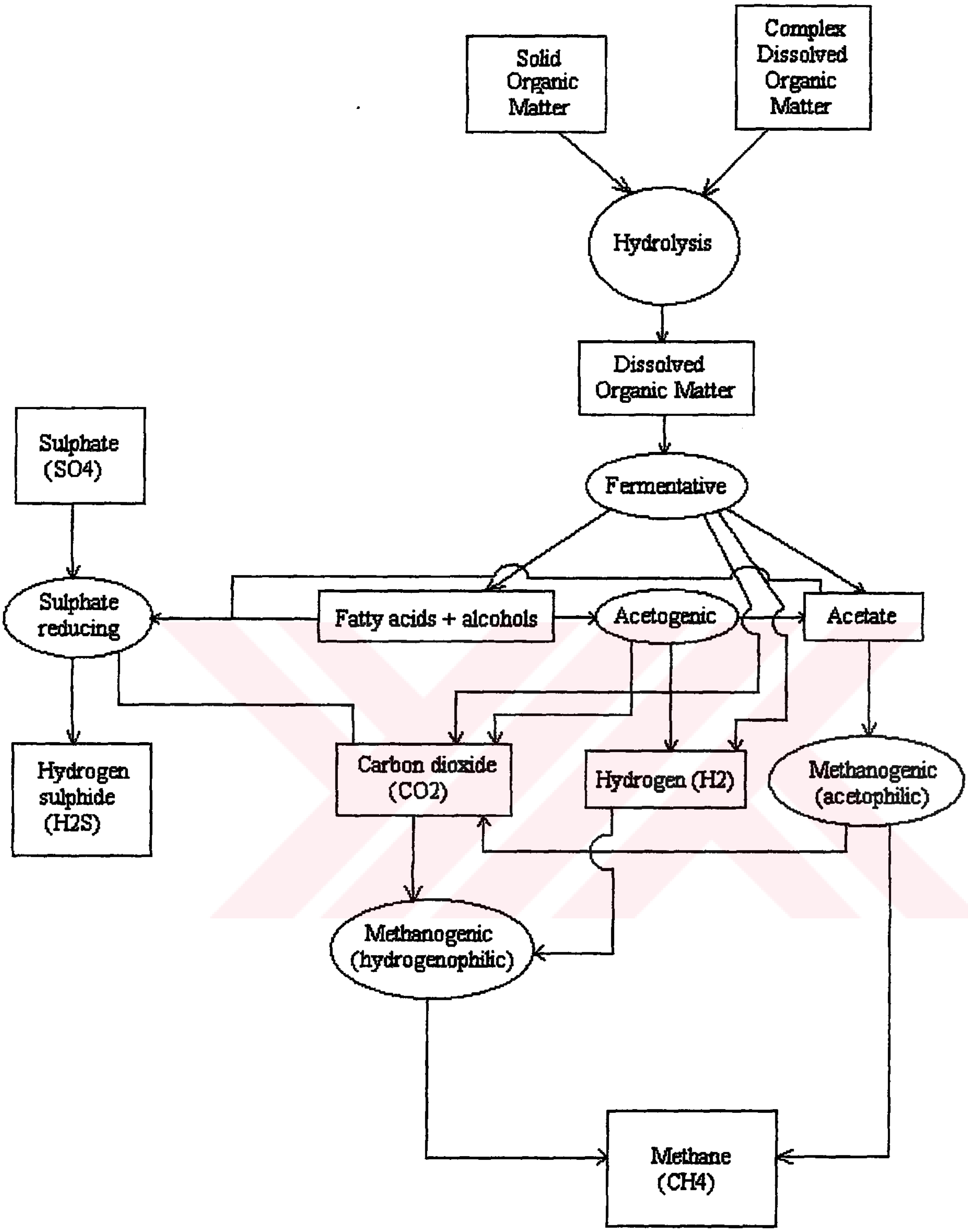


Figure 2.1. **Substrates and Major Bacterial Groups Involved in the Methane Generating Ecosystem. [7]**

While Christensen and Kjeldsen [7] stated that hydrolysis may prove to be the overall-limiting process in landfill environment, Farquhar and Rovers [9] stated that hydrolysis is not likely to be a rate limiting step in decomposition.

Acetogenic bacteria are a large heterogenic group of bacteria. However, there is controversy about microbial flora of acetogens, whether they are facultative or strictly anaerobic bacteria [9]. The acetogenic bacteria produce acetic acid, hydrogen, and also carbon dioxide if the volatile fatty acids being converted contains an odd number of carbon atoms. They may also convert aromatic compounds containing oxygen, while aromatic hydrocarbons apparently are not degraded [7].

The methanogenic bacteria are crucial to waste stabilization since they constitute a major final step in the decomposition process. Methanogens utilize only a narrow array of relatively simple substrates for growth and metabolism. Two main substrates are the hydrogen-mediated reduction of carbon dioxide and the aceticlastic cleavage of acetic acids. About two-thirds of methane is derived from acetate and one third from carbon dioxide. The methanogens can also convert formic acid and methanol. The methanogenic bacteria can be adversely affected by the accumulation of the hydrogen as well as the presence of electron acceptors such as nitrate and sulfate. Sulfate reducing bacteria can win over methanogens for available substrate (H_2, acetate) and hydrogen sulfide production can predominate over methanogenesis [10]. Although the methanogenic bacteria have a number requirements for growth, such as absence of oxygen and a pH of 6-8, they are a versatile group of microorganisms since there are species which are autotrophic, thermophilic and mesophilic [11].

Waste stabilization in anaerobic treatment is directly related to methane production. It is possible to mathematically predict the quantity of the methane that is going to be produced during the process of decomposition from the knowledge of the waste composition using the following formula [12]:

$$C_nH_aO_b + \left(n - \frac{a}{4} - \frac{b}{2}\right)H_2O \rightarrow \left(\frac{n}{2} - \frac{a}{8} + \frac{b}{4}\right)CO_2 + \left(\frac{n}{2} + \frac{a}{8} + \frac{b}{4}\right)CH_4$$

From this formula it can be shown that the ultimate oxygen demand of the waste being degraded is equal to the ultimate oxygen demand of the methane gas produced. This fact allows prediction of methane production in another way, that is from an estimate of COD or ultimate BOD stabilization using the following expression [12] :

$$1 \text{ lb } (1 \text{ kg}) \text{ BOD}_u \text{ or COD stabilized} = 5.62 \text{ ft}^3 \ (0.35 \text{ m}^3) \text{ CH}_4 \text{ (STP)}$$

2.1.2. Phases of Landfill Stabilization

Stabilization of landfill is the result of a number of physical, chemical and biological processes. A landfill is considered stabilized when the following criteria are met: (1) maximum settlement has occurred, (2) negligible gas production is occurring, and (3) leachate does not constitute a pollution hazard [13]. Many researchers [7, 9, 14, 15, 16] reported that municipal solid waste landfills progress through five sequential phases of stabilization: (1) Initial adjustment, (2) Transition phase, (3) Acid phase, (4) Methane fermentation phase, and (5) Maturation phase. Figure 2.2. illustrates the developments in gas and leachate composition during the five phases of landfill stabilization.

In Phase I, or Initial Adjustment Phase, solid waste undergo microbial decomposition as it is placed and soon after. Wastes are decomposed under aerobic condition, with the consumption of oxygen present in the refuse at the time of placement. Carbon dioxide is produced in approximate molar equivalents to the oxygen consumed. Very little displacement of nitrogen gas occurs [9]. Moisture begins to accumulate and first changes in environmental parameters are observed.

Upon the depletion of oxygen, waste decomposition enters Phase II or Transition Phase where anaerobic conditions prevail. As the landfill becomes anaerobic, reducing conditions are established and electron acceptors nitrate and sulfate are reduced to nitrogen gas and hydrogen sulfide. As a result of accumulated moisture inside the landfill field capacity is reached and first leachate is generated. The activity of fermentative and acetogenic bacteria results in a rapid generation of volatile fatty acids and carbon dioxide. As a result pH of the leachate starts to drop.

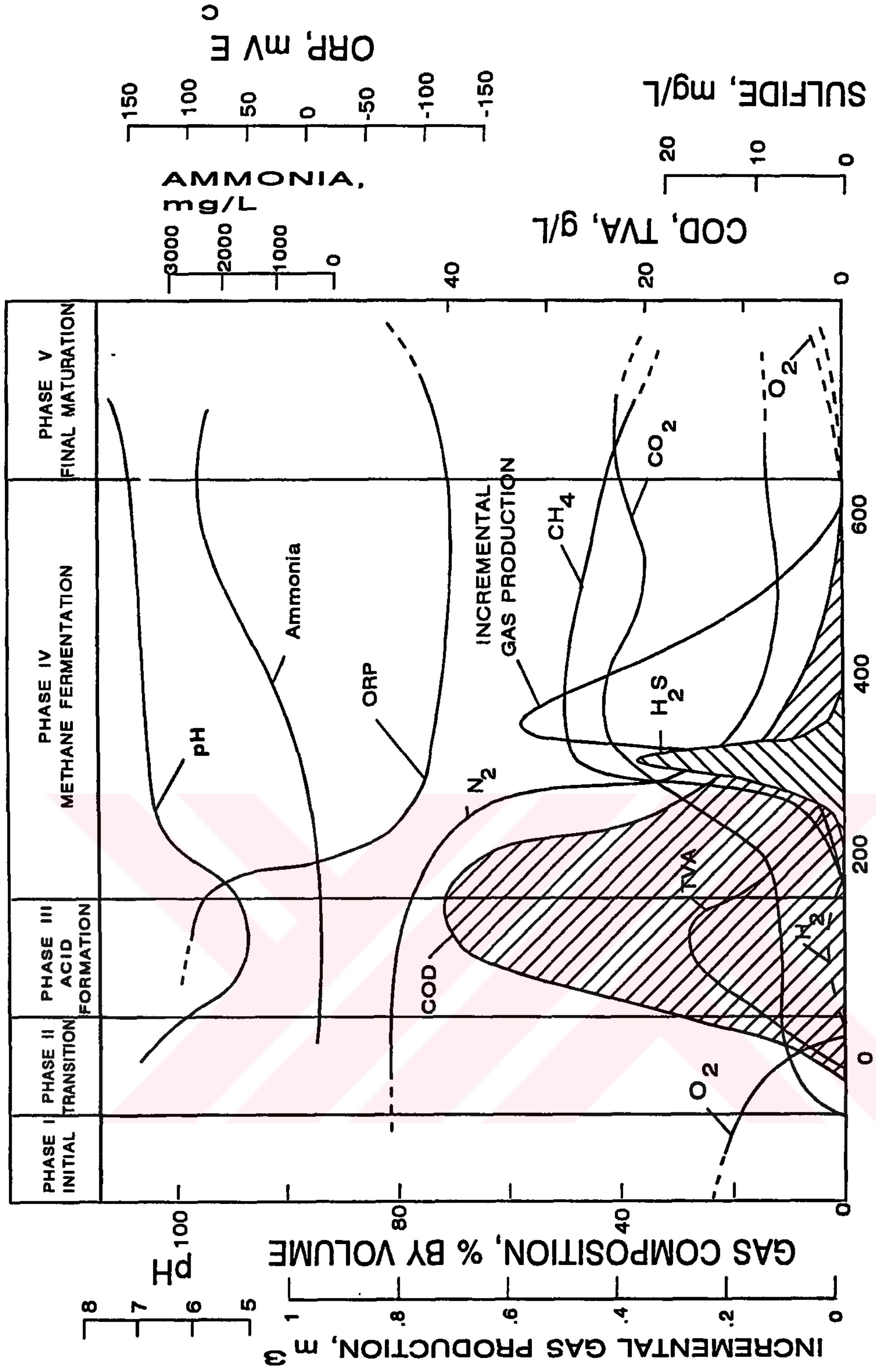


Figure 2.2. Changes in Selected Indicator Parameters During the Phases of Landfill Stabilization [6]

During the Phase III or Acid Phase, the microbial activity accelerates with production of organic acids and lesser amounts of hydrogen. First two steps of waste stabilization, hydrolysis and acidogenesis take place in this phase. The leachate pH continues to drop as a result of release of organic acid followed by mobilization and possible complexation of metal species. Many essential nutrients, such as nitrogen and phosphorus, are released and will be removed from the system unless leachate is recycled. Ammonia nitrogen concentration is increasing due to nitrate reduction and protein breakdown. The biochemical oxygen demand, the chemical oxygen demand, and conductivity of the leachate will increase due to dissolution of the organic acids in the leachate. As a result of aerobic solubilization, sulfate concentration will initially increase. With establishment of more reducing environment, sulfate will be reduced to sulfide [16].

Phase IV or Methane fermentation phase is characterized by stable methane production, resulting in a methane concentrations of 50-65% by volume [7]. Acids and hydrogen produced during previous phases are converted to methane and carbon dioxide. As a result pH of the system will rise to more neutral values of 6.8 to 8, and the BOD, COD, and conductivity will be reduced [14]. With high pH values, the concentration of heavy metals in leachate will be reduced as they become mobilized inside the waste matrix. Ammonia nitrogen will be reduced as a result of increased biological assimilation. Highly reducing environment in the landfill will favor complete sulfate conversion to sulfides [16].

In Phase V or Maturation phase, only refractory organics remains in the landfilled waste. The rate of landfill gas production diminish as a result of insufficient amount of nutrients and substrate removed in previous phases. Methane production rate cease with reappearance of small amount of oxygen and nitrogen. The aerobic zones will appear in the upper zones of landfill.

The rate and duration of these phases is dependent on physical, chemical and microbiological conditions developed in the each section of the landfill. However, it should be noted that this five stage stabilization process is applicable for homogeneous waste with sufficient availability of moisture and nutrients, not exposed to the inhibitory effects of toxic material. Real case landfills consist of cells of highly varying age and composition which may lead to the different environmental conditions established within the landfill.

In order to detect and describe the presence, intensity and longevity of each phase of landfill stabilization leachate and gas extracted from the landfill environment may be monitored for certain indicator parameters. According to Pohland et al. [15] indicator parameters include: pH, oxidation-reduction potential (ORP), chemical oxygen demand (COD), five day biochemical oxygen demand (BOD_5), volatile organic acids (VOA), nitrogen, and phosphorus. In addition to these, environmental conditions in the landfill may be further explained by: alkalinity, heavy metal concentration, conductivity, chloride concentration, nitrates and sulfates, and the presence of bacteria and viruses. Gas phase can be analyzed for daily production and composition, especially for methane and carbon dioxide concentrations.

The concentration of these parameters is directly related to the phase of landfill stabilization and the rate of dilution due to moisture influx. Dilution will tend to decrease concentrations during leachate analysis, but will not influence the total mass of leachate constituents in time and space.

2.1.3. Factors Affecting Landfill Stabilization

The factors affecting landfill stabilization include: temperature, pH, nutrients, moisture, toxic substances, and input solid waste characteristics.

2.1.3.1. Temperature

The process of landfill stabilization is strongly depended on temperature. Microbial reaction rates vary with different temperature conditions, ceasing at very low or very high temperatures. Two optimal temperature ranges are mesophilic (near 35°C) and thermophilic (55°C to 60°C) with decreasing rates between these optimum values [10]. Recommended temperature for process start-up and recovery from the upset is 35°C, while optimum temperature range for mesophilic anaerobic digestion is 30-32°C [4].

Hartz et al. [17] investigated the effect of temperature on methane generation in range from 21°C to 48°C. They founded that the optimum temperature for the methanogenesis is 41°C with methane production ceasing between 48°C and 55°C. Pfeffer [18] also conducted a series of experiments to determine the effect of temperature on solid waste decomposition process. He investigated the range from 35°C to 60°C at 5°C intervals, increasing the temperature by 1 to 1.5°C increments and found that the optimum mesophilic temperature is 42°C, while the optimum thermophilic temperature was at least 60°C, with methane production ceasing between 43 to 45°C. He noted that the changes in temperature as low as 1°C can result in ceasing of methane production. Farquhar and Rovers [9] reported that optimal mesophilic temperature for methane production was 37°C.

Temperature in landfills is not uniform and fluctuate as a result of air temperature variations and the extent and effectiveness of insulation provided by the landfill configuration. In a deep landfill with a moderate water flux, the flux of heat from the landfill to the surrounding environment is small due to insulating capacity of the waste and the heat generated by the anaerobic decomposition process may cause an exothermic temperature rise in the landfill. Landfill temperature of 30-45°C should be possible even in the temperate climates [7].

2.1.3.2. pH and Alkalinity

The maintenance of appropriate pH value in the landfill environment is crucial for the performance of microbial population. Most bacteria are very sensitive to concentrations of hydrogen or hydroxyl ions. Very low pH values resulting from excessive production of organic acids effect more methanogenic bacteria a fermentative bacteria that will continue to utilize organic portion of the waste and produce more acids. This will destabilize the environmental conditions in the system. Many species can grow well in pH range of 6.0-9.0, while optimum range is reported to be 6.4-7.2 [19]. Farquhar and Rovers [9] reported that optimal pH for methane production is near 7.0 and that deviations from this value result in a decrease of gas production. According to McCarty [20], optimum pH for efficient anaerobic treatment is between 7.0-7.2, with efficiency dropping at pH lower than 6.2.

Alkalinity represents the ability of system to buffer the effects of volatile and other acids which tend to depress the pH below desired level. High alkalinity concentration indicates that the system is safeguarded against pH fluctuations, while low alkalinity indicates that the high concentrations of acids may lower the pH so that the biological activity may cease. Pohland and Harper [16] in their literature review of landfill leachate constituents reported that alkalinity during acid formation phase my range from 140-9,650 mg/L as $CaCO_3$. On the other hand, Kotze et al. [19] reported that total alkalinity of 2000-3500 mg/L as $CaCO_3$ is desirable for well established anaerobic digestion process treating sewage sludge.

2.1.3.3. Nutrients

Efficiency of the anaerobic process is dependent on the adequate supply of the nutrients. In addition to the necessary macronutrients, nitrogen, carbon, and phosphorus, bacterial population also need small quantities of micronutrients such as iron, nickel, magnesium, calcium, sodium, barium, tungstate, molybdate, selenium and cobalt [10]. COD:N:P ratio is used to describe the nutrient requirement of the system. Christensen and Kjeldsen [7] reported that optimum COD:N:P ratio is 100:0.44:0.08. On average, the mixed waste landfill will not be limited by nitrogen and phosphorus, but insufficient homogenization of the waste may result in nutrient-limited environments. Nutrient sufficiency may be best assured through initial addition or leachate recirculation [16]. Pohland and Harper [16] reported that phosphorus concentrations may be limiting during the latter stages of biostabilization.

2.1.3.4. Moisture

Moisture content of the waste is one of the most important factors affecting the rate and nature of biological processes. The moisture content of the fresh waste as placed in landfill is reported to be between 20 to 40 percent on a wet weight basis [21]. Farquhar and Rovers [9] reported that maximum gas production occurs at moisture contents from 60 to 80 percent wet weight, while gas production ceased at moisture content ranging from 30 to 40 percent or less. The main effect of the increased water content, besides limiting oxygen transport from the atmosphere, is the promoted exchange of substrate, nutrients, buffer, dilution of inhibitors and spreading of microorganisms between the waste matrix [7]. Sufficient moisture content and necessary homogeneity of the waste can be provided with leachate recirculation.

2.1.3.5. Toxic Substances

The methane producing bacteria are known to be very sensitive to a number of toxic substances including: ammonia nitrogen, sulfide, heavy metals, and volatile acids.

Ammonia is produced as a result of decomposition of waste containing nitrogen. Ammonia nitrogen mainly exists as a ammonium ion at pH less than 7.2, or ammonia at higher pH values. Kotze et al. [19] reported that ammonia nitrogen content of at least 100 mg/L is assumed to be necessary for efficient digestion. Pohland et al. [15] stated that concentrations between 200-1500 mg/L have shown to have no adverse effects on anaerobic process, concentrations ranging from 1500-3000 mg/L were shown to have inhibitory effects at higher pH levels, and concentrations above 3000 mg/L were very toxic.

Sulfide in the solid waste originate from the reduction of sulfate under reducing conditions of about -50 mV to -100 mV or lower [14]. The growth and performance of methanogenic bacteria is inhibited at higher concentrations of oxidized sulfur. Oleszkiewicz et al. [22] reported that the sulfide threshold value is 200-300 mg/L, while Pohland [10] stated that the sulfide toxicity was observed at concentrations ranging from

200-1500 mg/L. The presence of heavy metals such as iron can lessen the toxic effect of sulfides by forming precipitates such as iron sulfide.

Some heavy metals are required in small amounts for efficient solid waste stabilization. Excess heavy metal toxicity is primarily due to disruption of enzyme structure and its function by the binding of metals with functional groups on proteins or replacing naturally occurring metals in enzymes. Although it is very difficult to establish the threshold value, the order of decreasing toxicity is known and is given as: Ni > Ca > Pb > Cr > Zn [10]. Heavy metals may react with sulfide, carbonate and hydroxide to form precipitates.

Acetic and propionic acids are the major volatile acids formed as a result of organic waste decomposition [23]. Although they serve as a food to methanogens, at high concentration they are inhibitory to the digestion process, even if neutral pH is to be maintained. McCarty and Brosseau [24] reported that concentration of acetic and butyric acids to 6000 mg/L, both individually and in combination have rather a stimulatory effect on digestion process, providing neutral pH is maintained. They also reported that a sudden increase in propionic acid concentration to levels of 3000 to 8000 mg/L hinders gas production for up to one or two weeks, after which acclimation occurs and process returns to normal. McCarty and McKinney [25] reported that the decreased activity of methanogens is not actually due to volatile acid toxicity but due to sodium salts toxicity from the cation of the base added to neutralize the acids.

2.1.3.6. Input Solid Waste Characteristics

The composition of the solid waste landfilled is one of the crucial factors influencing waste stabilization. By its nature, waste may contain materials which are toxic or inhibitory to the microbial population responsible for waste stabilization, or its nutrient concentrations may be insufficient retarding activity of microorganisms. The physical state of refuse, especially its size and surface area is likely to influence decomposition rates [9,16]. The shredding of the waste was found to increase the rate of decomposition and to lead more quickly to methane production [26].

2.1.4. Enhancement of Landfill Stabilization

One of the characteristics of the landfills is the long stabilization times they require. Stabilization may be defined as the state of relative physical, biological, and chemical stability achieved inside the landfill [27]. Without optimization of the conditions inside the fill it may take decades to achieve the stabilization.

Some advantages of accelerated stabilization are: (1) organic concentrations of leachate will be up to two times lower and biological treatment will be much cheaper, (2) gas production will be enhanced with higher methane concentrations, (3) reclamation of the landfills will be less problematical, and (4) settling process will take place earlier [28].

Stabilization of the landfill may be accelerated if microbiological processes in landfills could be enhanced. The enhancement of the microbiological processes can be achieved by providing environment favored by the microbial population, thus allowing them to growth and reproduce faster. Stabilization of the landfill may be accelerated using one of the following techniques; leachate recirculation, pH control/buffer addition, nutrient addition, and sludge addition [28].

Leachate Recirculation involves collection, containment, and recirculation of the generated leachate into and through the landfilled waste matrix. Laboratory and pilot scale studies have shown that leachate recirculation accelerates the stabilization of waste, enhances gas production and improves leachate quality [29]. Recirculation provides a means of optimizing environmental conditions within the landfill to enhance stabilization of landfill contents, as well as treatment of moisture moving through the fill. For those landfills that do not have inexpensive leachate disposal at a nearby wastewater treatment plant, leachate recycle can save considerable money in leachate management. Pacey [30] reported that leachate recirculation enhances methane gas generation. Stegmann and Spendlin [28] in their laboratory and full scale test found out that the controlled leachate recirculation should be practiced to increase moisture content in area where precipitation is less then 750-800 mm/year. They noted that leachate recirculation resulted in evaporation loss of leachate, and that leachate stabilized by recirculation require treatment with minimum energy input, mainly being based on nitrification processes. Pohland [31] found out that recirculation of leachate through a landfill promotes a more rapid development of an active methanogenic population, increases the rate of biological stabilization of organic pollutants in the waste matrix and leachate, and dramatically decreases the time required for stabilization. Onay and Pohland also reported that leachate recycle enhanced and accelerated conversion and stabilization in landfill simulating reactors by increasing the uniformity of moisture, substrate and nutrient distribution [32]. Leachate recirculation is proved to be a very effective means for acceleration of landfill stabilization when used in combination with other techniques, such as pH buffering or addition of sludge and/or nutrients. In his experiment, Pohland [31] reported that sludge seeding and pH control in combination with leachate control further enhance treatment efficiency so that the time required for biological stabilization of pollutant in leachate can be reduced to a matter of months rather than years. Leuschner [33] in his laboratory scale experiments found that leachate recirculation with addition of buffer, nutrients and microbial inoculum enhance methane production and improve leachate quality.

pH control/buffer addition; One of the most important environmental requirements for efficient anaerobic waste treatment is a proper pH. While optimum pH is given to be between 7.0 - 7.2, at pH below 6.2, efficiency of the anaerobic process drops off rapidly and acidic conditions become toxic to methanogenic bacteria [20]. Therefore, maintenance of neutral pH is very important factor for the efficient anaerobic waste decomposition process. The positive effects of pH control or buffer addition have been well documented in several researches [4, 31, 33] However, there are also some contradictions in the reported results. While Pohland [31] and Leuschner [33] reported that buffering of leachate prior to recirculation establish a proper pH within the reactor and result in rapid methane formation, Stegmann and Spendlin [28] reported that addition of NaOH to keep pH at 7.0 did not positively effected the system. They speculate that the result they found may be different due to different test conditions. pH control within the landfill may be achieved by adding a solid buffer materials such as lime or calcium carbonate or by neutralizing the pH of leachate prior its recirculation [28].

Nutrient addition; addition of major nutrient such as nitrogen and phosphorus is reported to be stimulatory for the enhancement of bioegradation process. In the systems with nutrient deficiency, external addition of nutrient effectively shorten the lag phase [33]. However, neither Pohland and Harper [16] nor Leuschner [33] did not observed any visible effects of nutrient addition on gas production. Although municipal solid wastes generally contain necessary nutrients, for landfill with nutrient deficiencies Pohland and Harper suggest initial nutrient addition or leachate recirculation as a effective method for control over stabilization rates and gas production.

Sludge addition; despite some potential adverse effects that sludge addition may have on landfill environment (heavy metal content, pathogenic organisms etc.) there are some major benefits that can be derived from this practice. Watson-Craik and Sinclair [34] reported that sludge addition decreases the period before the onset of methanogenesis and optimizes methanogenic activity through the addition of nutrients, inoculum, and moisture, therefore facilitating the development of active methanogenic population. Furthermore, sludge addition has proved to lead to more rapid landfill stabilization. Pacey [30] reported that addition of sludge enhanced methane generation rates while Pohland [31] suggest that initial sludge seeding may further accelerate landfill stabilization by introducing active bacterial population. However, Leckie et al. [13] do not recommend septic tank sludge seeding without leachate recycling with pH control. Güleç [35] proved that the addition of anaerobically digested sludge is beneficial for the rate and extent of waste stabilization. The sludge to waste ratio of 1:4 provides most enhanced and efficient degradation of solid waste as measured by highest methane generation rates, highest COD removal and other leachate indicative parameters.

2.2. Leachate Generation and Characteristics

Tchobanoglous et al. [14] defined leachate as liquid that has percolated through solid waste and has extracted dissolved or suspended materials. Initiation of leachate production is related to the exceed of field capacity, that is defined as the maximum moisture content that a porous medium can retain against gravity before it starts producing continuous downward flow [36].

Leachate is composed of the liquid that enters the landfill externally, such as surface drainage, rainfall, groundwater, and water from the underground springs, and the liquid produced from the decomposition of the solid waste. Factors effecting the quality and quantity of the landfill leachate are: (1) annual rainfall, (2) runoff, (3) infiltration, (4) evaporation, (5) transpiration, (6) freezing, (7) mean ambient temperature, (8) waste composition, (9) waste density, (10) initial moisture content, and (11) depth of the landfill [13]. Although it is well documented that leachate quality depends on meteorological conditions and the hydrologic properties of the cover and waste material [13, 26, 37, 38, 39], the information given in the literature related to the seasonal and water flux depended leachate quality are contradictory. While Rovers and Farquarh [37] reported that increased infiltration will result in increased leachate strength, monitored by the increase in COD, VDS, NH_3-N, Org-N, Ca, Mg, Fe, and Cl, and decrease in alkalinity and pH, Leckie et al. [13] reported that continuous flow-through of water will reduce leachate strength. In lysimeter tests, Ham and Bookter [26] found that increased COD concentrations coincided with winter thaws and spring rains, while Akesson and Nilsson [39] reported that COD concentrations decrease with increasing flow rates.

Leachate characteristics change as process of landfill stabilization proceed. Leachate can be characterized as a "young" and "old" leachate depending upon the phase of landfill stabilization.. Acidic phase of landfill stabilization is characterized with young leachate containing high concentration of organic pollutants. As landfill becomes older, organic content tends to decrease and leachate produced is named "old" leachate [40]. Characteristics of the leachate from old and young landfill are given in the Table 2.2.

Factors affecting leachate generation include influx of ground and surface waters, moisture generated from waste stabilization as well as initial moisture content of the waste encapsulated [6]. The potential for leachate formation may be predicted by preparing the water balance on the landfill. Volume of water in excess of the moisture holding capacity of the waste matrix is defined as a volume of potential leachate that is going to be produced [14]. Water balance computation is based on the traditional hydrologic approach and is given by [36]:

$$\text{Leachate} = P - SR - SMS - AET$$

Table 2.2. Typical Data on the Composition of Leachate from New and Mature Landfills [14]

	Value, mg/L[1]		
	New Landfill (less than 2 years)		
Constituent	**Range**	**Typical**	**Mature Landfill (greater than 10 years)**
BOD_5	2000-30,000	10,000	100-200
TOC	1500-20,000	6,000	80-160
COD	3,000-60,000	18,000	100-500
Total Suspended Solids	200-2000	500	100-400
Organic Nitrogen	10-800	200	80-120
Ammonia Nitrogen	10-800	200	20-40
Nitrate	5-40	25	5-10
Total Phosphorus	5-100	30	5-10
Ortho phosphorus	4-80	20	4-8
Alkalinity as $CaCO_3$	1000-10,000	3000	200-1000
pH	4.5-7.5	6	6.6-7.5
Total Hardness as $CaCO_3$	300-10,000	3500	200-500
Calcium	200-3000	1000	100-400
Magnesium	50-1500	250	50-200
Potassium	200-1000	300	50-400
Sodium	200-2500	500	100-200
Chloride	200-3000	500	100-400
Sulfate	50-1000	300	20-50
Total iron	50-1200	60	20-200

[1] Except pH, which has no units

where,
P: precipitation,
SR: surface runoff
SMS: change in soil moisture storage,
AET: actual evapotranspiration.

Precipitation corresponds to the amount of water entering the landfill from above, mostly in the form of rainfall. Evapotranspiration is combined evaporation from the plant and soil surfaces and transpiration from plants, and therefore represents the transport of water from the earth back into the atmosphere. Surface runoff represents water that flows directly from the landfill, while change in soil moisture storage may be due to the water that flows from the surrounding area into the landfill, such as groundwater or aquifer.

As reported by Korfiatis and Demetracopoulos [36] empirical expressions used for the computation of water balance pose certain problems since no actual process of moisture transport through the waste matrix is taken into account.

There are several other approaches used to predict leachate generation in the landfills. One of these is Soil Conservation Service (SCS) procedure for computation of surface runoff and its updated version prepared by EPA called HELP used for simulation of flow that percolates through the soil cover. Modified Penman method is used to estimate evapotranspiration [36]. In addition to these, U.S. EPA hydrologic simulation model (HSSWDS) and MORECS comprehensive meteorological model are used to predict the leachate generation rates in landfills. PITTLEACH-2 mechanistic model is developed to simulate leachate quantity and quality, as well as biogas generation [6].

2.3. Leachate Management Strategy

Two fundamental ways of treating the leachate generated from the landfills are *ex situ* and *in situ* leachate treatments. *Ex situ* treatment involve single pass leaching with leachate containment, collection and external treatment, while *in situ* treatment involve leachate containment, collection, and recirculation back into and through the landfill [15].

2.3.1. Single Pass Leachate Management Strategy

Ex situ or single pass leachate management strategy is employed at nearly all full scale operating landfills where produced leachate is managed. Landfills are operated to minimize the entry of moisture, therefore to reduce volume of leachate produced, and reduce formation of soluble pollutants. Formed leachate is collected and treated to remove organic and inorganic contaminants prior to ultimate disposal. Treatment of the single pass leachates may include biological processes to remove organic fraction followed by physical chemical treatment to remove residual organics, inorganics, color, and/or odor [15]. However, leachate composition and quantity vary greatly depending on the several factors including chemical and biological activities, moisture, temperature, pH, and age of the landfill [38]. For that reason it is very difficult to recommend specific treatment process, since treatment plant designed to treat a leachate from the new landfill would be quite different from one designed to treat a leachate from a mature landfill. Furthermore, leachate produced in one landfill is the mixture of leachates derived from the solid waste of different ages. The type of treatment to be selected depends on the leachate characteristics. Leachate containing high TDS concentrations (greater than 50,000 mg/L) may be difficult to treat biologically, while high COD values favor anaerobic treatment due to its lower cost. High sulfate concentrations may limit anaerobic treatment because of the production of odors [14].

For removal of biodegradable fraction of leachate, biological treatment proved to be more efficient than physical-chemical treatment. Leachate from the new landfills, containing high concentrations of organic constituents may be well treated with aerobic biological processes. Robinson and Maris [41] found that aerobic biological treatment of leachate at low temperatures removed BOD more that 98 percent and COD more than 92 percent. Together with organics removal, ammonia nitrogen and metal removal was observed. Ammonia removal was largely from incorporation in biomass during removal of organic material. Pohland and Harper [16] reported that, given sufficient residence time, biological processes achieved 90 to 99 percent organics removal (BOD_5 and COD) with 90 percent ammonia nitrogen conversion for residence time greater of 10 days. For residence time of 6 to 10 days 60 to 80 percent nitrification was achieved. Aerobic biological processes are also efficient in heavy metals removal. Zinc, chromium, and iron are reported to be removed at efficiencies greater that 90 percent while copper, lead, cadmium, and nickel at efficiencies of 50 to 90 percent. Activated carbon adsorption yield effluent BOD_5 concentrations less than 50 mg/L.

Except activated carbon adsorption, other physical-chemical treatments were proved to be inefficient for the removal of organics. However, physical-chemical treatments were successfully applied to treat effluents from the biological treatment processes. Reverse osmosis remove high percentage of organics, activated carbon (GAC or PAC) and ion exchange remove successfully copper, lead and nickel, as well as iron, zinc, chromium, manganese, calcium, and manganese[16]. The flow charts of typical leachate treatment systems for leachate from young and old cells are given in the Figure 2.3. [42].

2.3.2. Leachate Recirculation Management Strategy

Landfills operated in such a manner to minimize environmental impacts with optimizing waste degradation are called *bioreactor landfills* [29]. Increasing attention is being given to leachate recirculation in municipal solid waste landfills as an effective way to enhance microbial decomposition of the biodegradable solid waste. With leachate recirculation, landfill can be used as relatively uncontrolled anaerobic filter to treat leachate, provide accelerated stabilization, and reduce volume of leachate by maximizing evaporative losses during recirculation [41].

As the modern sanitary landfills, bioreactors are equipped with liners and leachate and gas collection systems. However, certain modifications in design and operational criteria are made in order to optimize waste degradation. For example, the bottom liner system is designed to intercept the additional flow contributed by leachate recirculation and the gas management facilities is operated to control increased gas production. Lecahate recirculation devices compatible with daily operation and closure requirements are employed. Furthermore, leachate management is carefully planned to ensure adequate supply for recirculation during dry weather conditions or during wet weather periods. The elements of a typical bioreactor landfill are given in the Figure 2.4. [29].

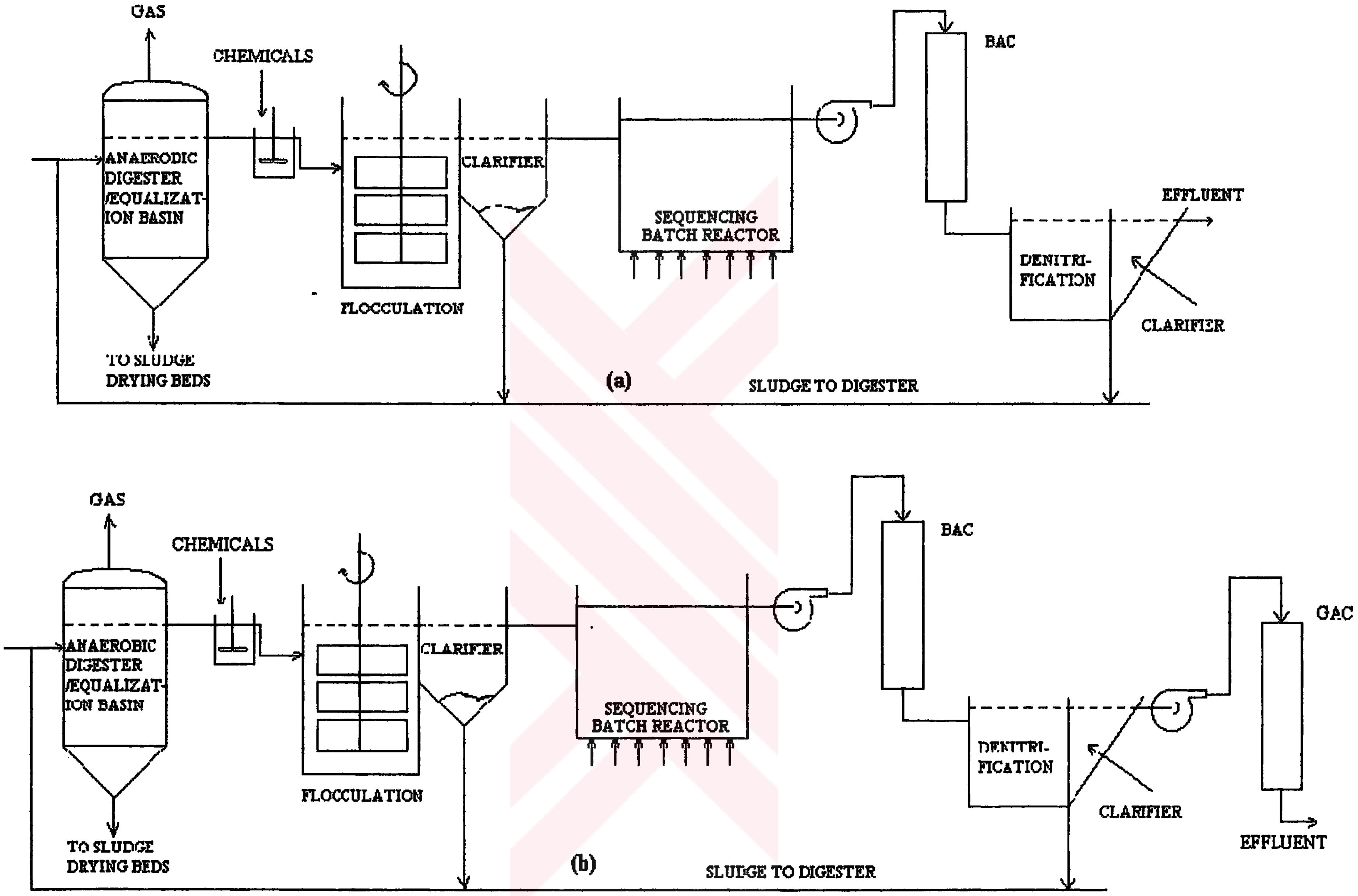


Figure 2.3. Flow Chart for Complete External Leachate Treatment: (a) young to medium age landfill, (b) old landfill. [42]

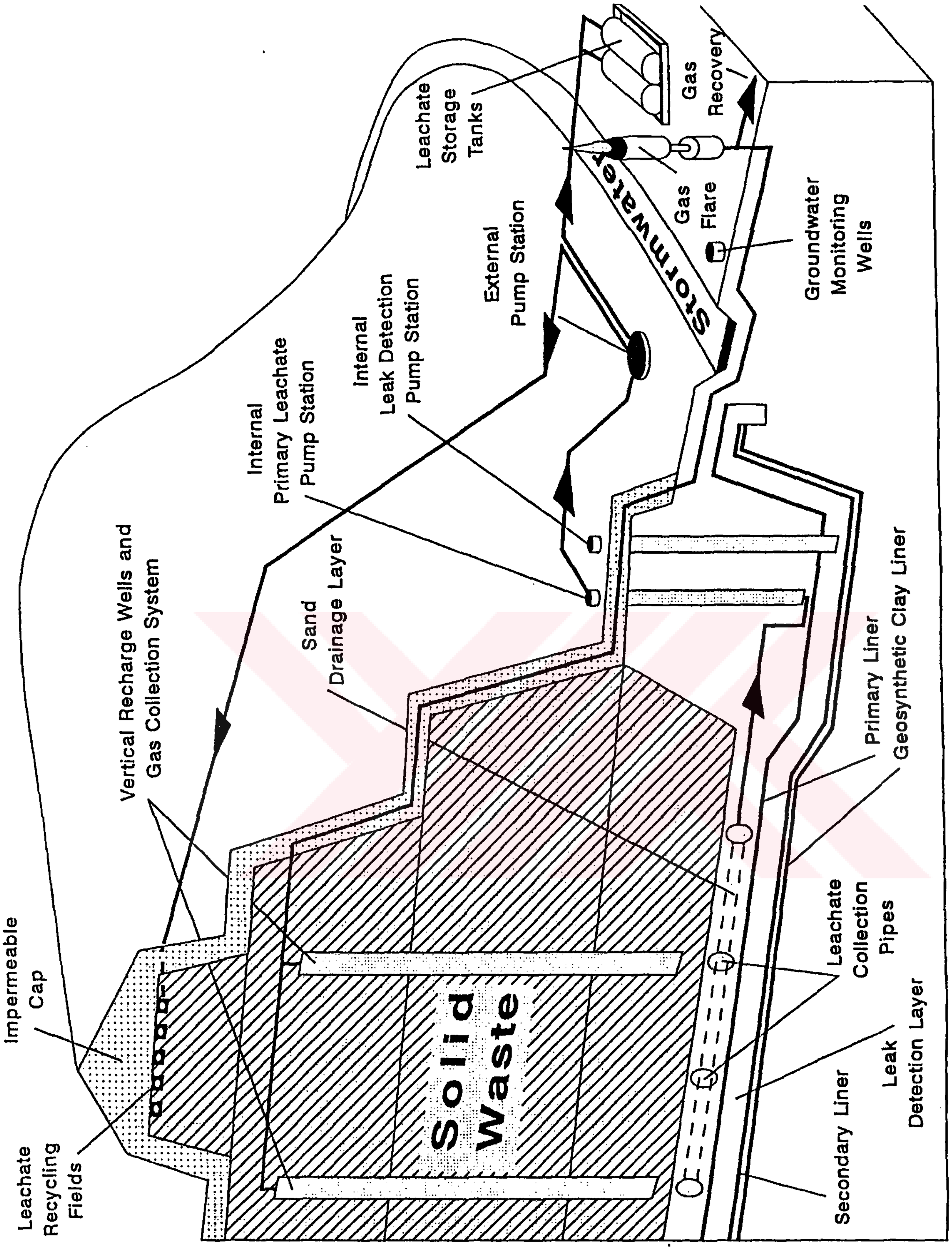


Figure 2.3 Elements of Bioreactor Landfill [6]

In situ treatment of leachate has been demonstrated to be successful on pilot and full scale. Several researchers [3, 6, 13, 15, 16, 21, 26, 27, 28, 29, 31, 32, 41, 43, 44, 45] have documented that recirculation of leachate through solid waste provided increased moisture content and resulted in rapid decline in the strength of leachate produced, accelerating the rate of landfill stabilization. Leachate produced is contained and recirculated back into the system thus allowing microbial population established inside the system to have enhanced and prolonged contact with moisture, substrate, and nutrients, needed for growth and reproduction. Leachate recirculation provided more uniform and homogenous environment for the microorganisms accelerating their activity and fasten waste decomposition. As a result of leachate recirculation, time required for landfill stabilization may be reduced from 15 to 20 years to 2 to 3 years [16].

In order to maximize waste stabilization, leachate recirculation frequency is a parameter that carefully must be selected. Recirculation frequency is usually dictated by the volume of leachate accumulated in the storage facilities. If too much leachate is recirculated, problems such as saturation, ponding, and acid-stuck conditions may occur. Saturation is indicative of stagnant conditions, detrimental to the landfill processes. It is very important to introduce leachate slowly before the onset of methanogenesis, since high flow rates may deplete buffering capacity and remove methanogens. However, once the gas production is well established, leachate can be recirculated more frequently and at greater flow rates [29].

As reported by Leckie et al. [13], water added initially to increase moisture content of waste, accelerate the landfill stabilization. Furthermore, he found out that continuous flow-through of water accelerates stabilization of waste material, flushes out soluble materials, and increase the rate of settlement. Chugh et al. [21] studied the effect of recirculated leachate volume on waste degradation. Volume of recirculated leachate was selected to be 2 percent, 10 percent, and 30 percent of the initial volume of waste bed in the reactors. He observed that system start up at low moisture content is feasible and, that waste decomposition improve with increase in moisture flow. This findings are contributed to the increased flushing and dilution of the inhibitory products, maintenance of favorable environmental conditions by uniform distribution of moisture, and addition of higher quantities of inoculum.

In his laboratory scale experiment studying leachate recirculation feasibility in providing leachate treatment, Pohland [31] reported that leachate recirculation accelerates decomposition process as characterized by low COD/TVA concentrations. Furthermore, he observed that leachate recirculation with pH control gave the best performance with rapid decline in COD and TVA concentration. His findings are confirmed by work of Tittlebaum [3] who reported that leachate recirculation with pH control accelerated biological stabilization reducing time required for stabilization. Onay and Pohland [32] also reported that leachate recycle enhanced and accelerated conversion and stabilization in landfill simulating reactors by increasing the uniformity of moisture, substrate and nutrient distribution.

There are several full scale studies found in the literature, demonstrating the successful application of leachate recirculation treatment. One of these studies was done in former federal Republic of Germany, where 13 landfill were practicing leachate recirculation using spray irrigation, spray tankers, and horizontal distribution pipes [45]. It was observed faster reduction of BOD and COD in landfills commencing leachate recirculation few years after beginning of landfilling operations, without any increase in salts or heavy metals attributable to leachate recirculation. In landfills where waste is placed in thin layers, leachate was observed to have very low strength.

In study conducted by Townsend et al.[43], leachate recirculation is practiced on full scale in Alachua County Southwest Landfill in North-Central Florida. Leachate was recirculated first using infiltration pond leachate recycle system. Leachate recirculation rate was 230 m^3/d over the area of 11 ha. As a result of gas and leachate analysis it was concluded that leachate recirculation increased moisture content of waste matrix and accelerate the stabilization by providing conditions suitable for biological stabilization. Leachate quality was reported to be lower compared to the areas without leachate recirculation. Furthermore, waste ultimate methane yield indicated that stabilization was greater in the area receiving recirculated leachate.

In another study performed in Sonoma County in California [13], leachate recirculation was practiced at rate of 500-1000 m^3/d over the cell area of 225 m^2. As a result of investigation, it was concluded that leachate recycle established active anaerobic microbial population in the fill, and increased the rate of biological stabilization as evidenced by COD and BOD reduction. Furthermore, it was found out that leachate recirculation used landfill volume as an uncontrolled anaerobic digester for effective anaerobic treatment of its own leachate.

Full scale study done in Seamer Car Landfill in United Kingdom once more confirmed the findings form the other full scale leachate recirculation studies [29]. Approximately 300 m^3 of leachate was recirculated for five months in 1980, and 3780 m^3 and 11,400 m^3 in 1981 and 1982, respectively, over an area of 1 ha. Remaining 1 ha of the landfill served as a control area. Although they faced with problems related to surface ponding, saturated zones, and perched areas within the landfill, they observed that leachate recirculation rapidly reduced organic strength of leachate by increasing waste moisture content.

Leachate recycle management strategy converts the landfill into an anaerobic reactor that behave as a treatment facility for its own leachate. Leachate undergoes biological treatment inside the landfill due to microorganisms present in the waste matrix. Onay and Pohland [32] found out that in reactors operated with leachate recirculation 95 percent of nitrogen conversion is achieved by *in situ* nitrification and denitrification. Leachate from the landfill stabilized by the recirculation is characterized by low biodegradable organic matter, BOD/COD ratio less than 0.1, high ammonia concentration, and low metal concentration [40]. Pohland and Harper [16] reported that effluents from the leachate recycle studies had typically 30 to 350 mg/L BOD_5, 70 to 500 mg/L COD, 4 to 40 mg/L iron and less than 1 mg/L zinc. Pohland et al. [44] reported that leachate recirculation provide *in situ* physical-chemical process for immobilization of heavy metals and reduction of potential for external environmental damage.

Leachate recirculation offers an alternative treatment method for reducing volume and organic content of the leachate, however, it cannot be complete answer to leachate treatment prior its final discharge. Additional chemical-physical treatment should be employed to obtain leachate with characteristics acceptable for final discharge. As reported by Diamadopoulos [40] coagulation-precipitation studies yielded maximum COD removal 56 percent for iron, 39 percent for aluminum, and 18 percent for lime at optimum pH of 4. Powdered activated carbon adsorption at pH 7 resulted in final COD of 300 mg/L, while air stripping of ammonia was very efficient, removing 95 percent of ammonia.

Leachate recirculation provides enhanced gas production rates. Leachate recirculation increase moisture content of the waste matrix, and establish the environment favored by methanogenic bacterial population. As a consequence, higher methane concentrations may be obtained, balanced with carbon dioxide and smaller amounts of hydrogen, oxygen, nitrogen, and traces of other gases. According to Pacey [46] leachate recirculation enhance methane gas generation. Chugh et al. [21] reported that with increased moisture content rate of methane production increase by 25 to 50 percent. In their experiment they obtained the methane yield of 0.13 m^3/kg VS added. Townsend et al. [43] reported that methane concentrations in landfill gas from “wet areas” reached 50 to 57 percent. Landfill gas with high methane concentration is a potential fuel and may be recovered and used for the generation of heat or electricity. Landfill gas recovery operation include gas cleanup and sale to existing gas pipelines, the operation of gas-fired electrical generators, and the use of the gas as a vehicle fuel [29].

3. MATERIALS AND METHODS

3.1. Reactor Experiment

3.1.1. Configuration of the Simulated Landfill Reactors

The simulated landfill reactors for single pass leaching and leachate recycle operations were constructed in the laboratory with features presented in Figure 3.1. and Figure 3.2., respectively.

The reactors were constructed using lengths of PVC pipe columns with length of 1m and a diameter of 0.35 m. PVC flanges were used both at the top and bottom of the reactors to provide support for the top and bottom lids. A coating of silicon, was applied to all connections and joints to ensure that the units are water and gas tight.

A 2 cm diameter PVC tee at the center of the bottom lid facilitated the installation of a leachate collection and sampling line. 0.75 cm diameter Masterflex® hose attached to the tee was used to transfer leachate to 18 L plastic container or to leachate sampling port.

A 2 cm diameter tee at the center of the top lid and a 1 cm diameter hole, located 14 cm radially apart from the center hole, functioned as liquid addition and gas sampling ports, respectively. 0.75 cm Masterflex® hose, attached to one end of the tee, was used for liquid addition. In case of the recycle reactor, 0.75 cm Masterflex® hose attached to other end of the tee was connected to the leachate plastic container and functioned as a leachate recycle line. In case of the single pass reactor, other end of the tee was capped with rubber septum and sealed with silicon. A PVC tee was placed in the 1 cm diameter hole. One end of the tee was attached by 0.75 cm Masterflex hose. The hose was connected to the leachate glass container and functioned as a pressure balance and gas collection line, while the other end of the tee

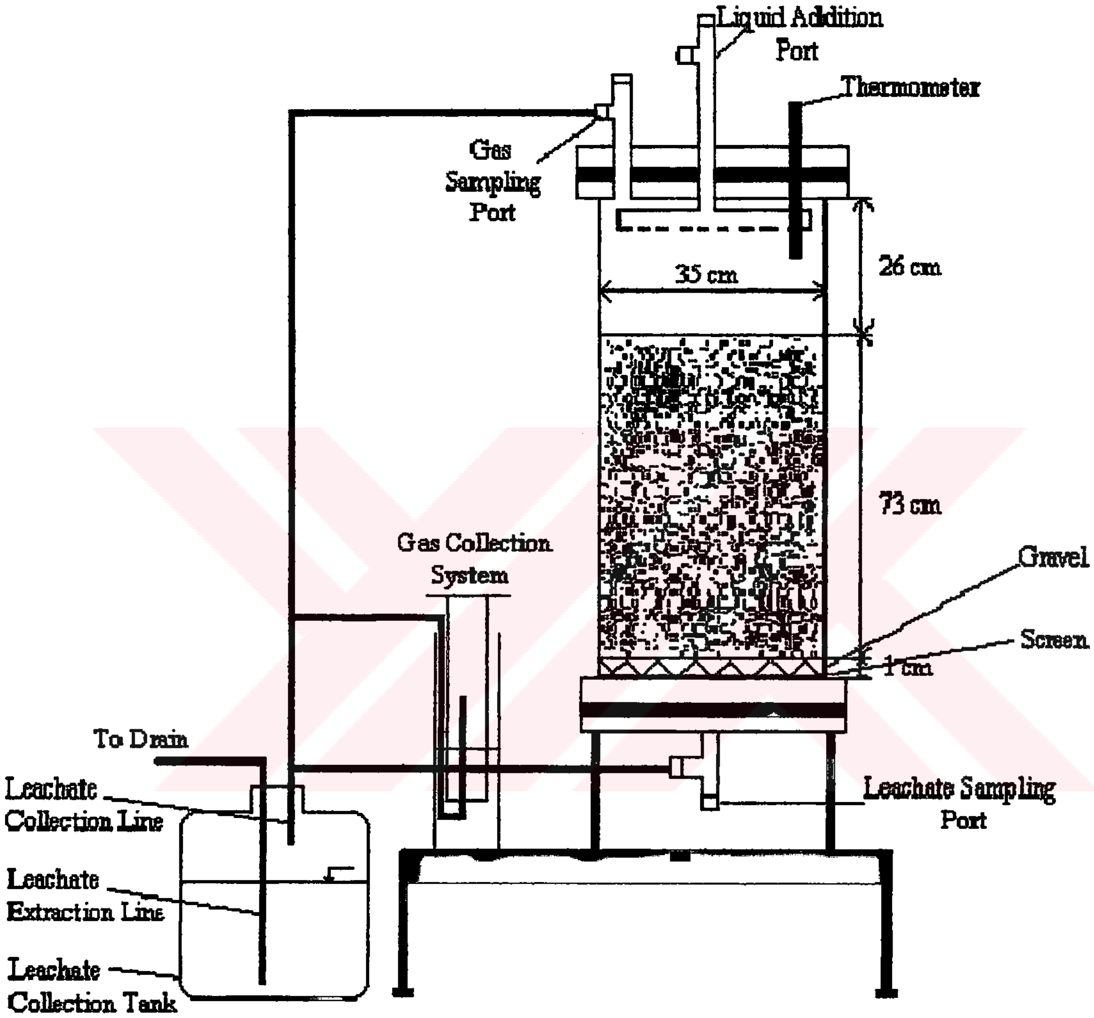


Figure 3.1. Lab-Scale Simulated Landfill Reactor with Single Pass Leaching

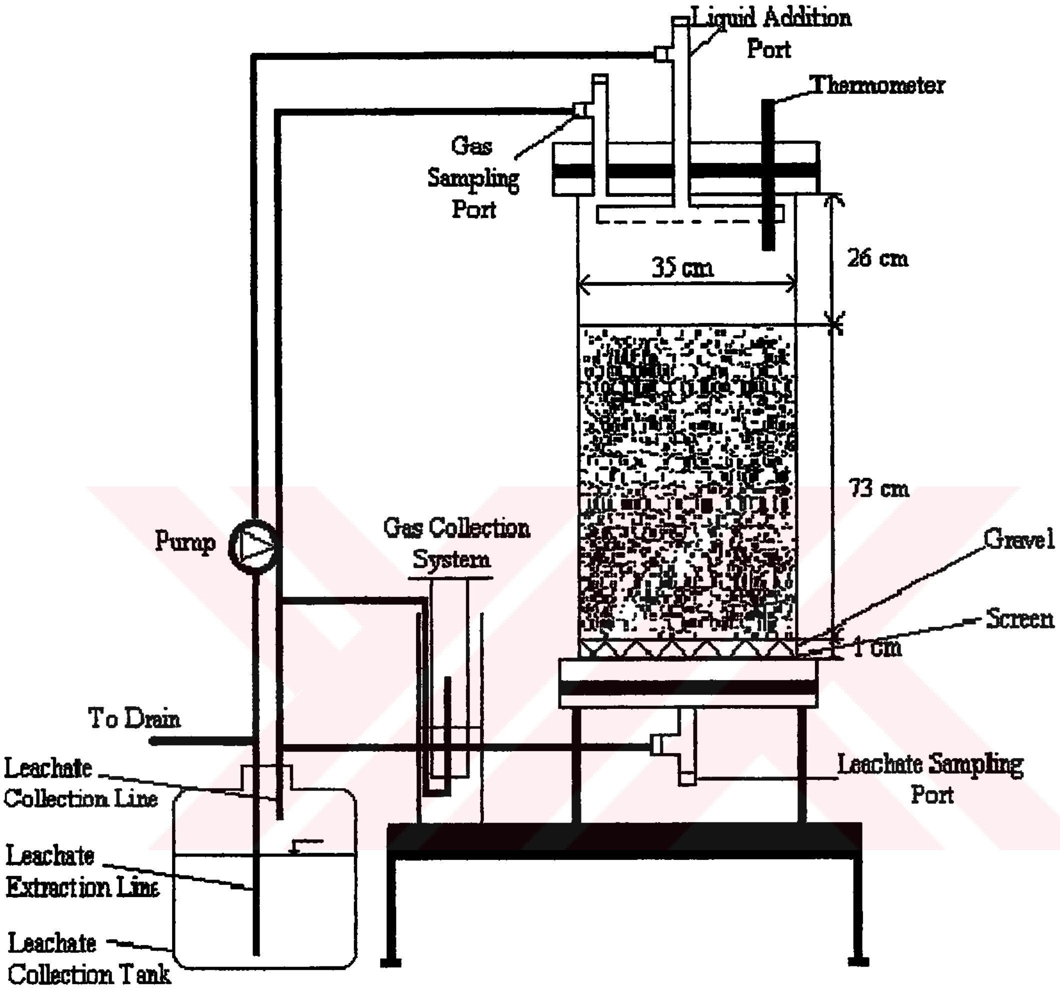


Figure 3.2. Lab-Scale Simulated Landfill Reactor with Leachate Recycle

was capped by a rubber septum and functioned as a gas sampling port.

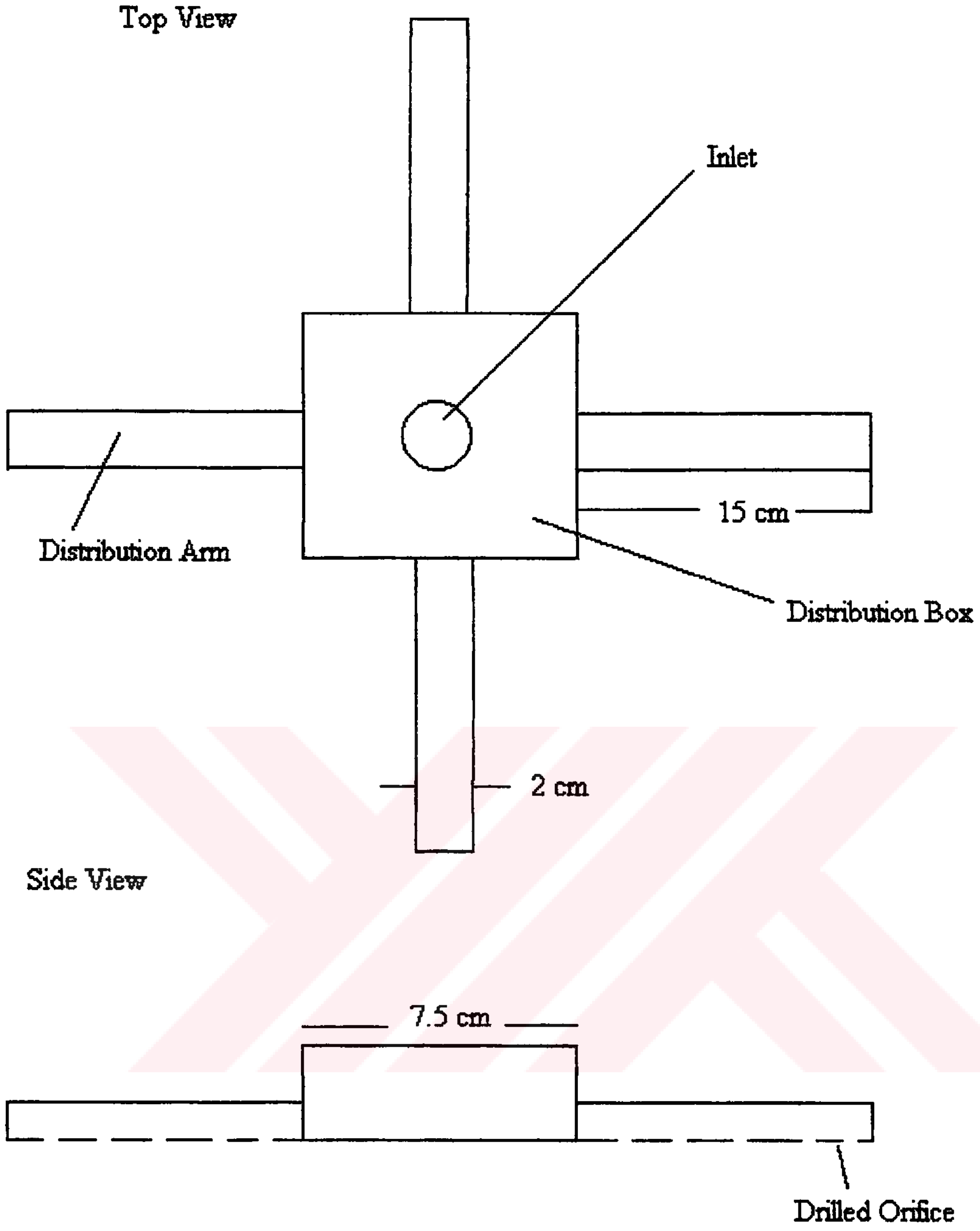
A leachate distribution system was constructed at the center of the top lid to provide uniform leachate distribution onto the waste matrix. As indicated in Figure 3.3., a distribution box made of PVC sheet was used for leachate distribution purposes. Three square PVC sheets with dimensions of 7.5 cm long, 7.5 cm wide, and 0.8 cm thick were glued together to form the distribution box with 2 cm holes on five faced. Four 2 cm diameter PVC pipes with a length of 15 cm attached to PVC end-caps were assembled with the box to form distribution arm array. Five 0.5 cm holes drilled with 2.5 cm spacing were placed along the entire length of each manifold to provide an even liquid distribution system.

All purpose thermometer at the top lid, located 10 cm radially apart from the liquid addition port, was used for the determination of daily temperature changes inside the reactors.

A ISMATEC S460 MINI pump was used to deliver leachate collected in the plastic container to the recycle reactor. The suction side of the pump was extended to the bottom of the leachate container, whereas the discharge side was connected to the liquid addition port of the recycle reactor.

The inside bottom of each reactor was filled by all purpose landscaping gravel to form a leachate drainage zone. The gas produced from reactors was collected and measured using the inverted cylinder technique. This technique utilized one 1 L glass cylinder inverted and placed into one 2 L plastic cylinder which was filled with confining solution (20% Na_2SO_4 in 5% H_2SO_4) [47]. The inner cylinder was lifted until the level of the confining solution in both cylinders equilibrated, and the amount of gas produced in a certain period was indicated by the volume occupied in the inner cylinder.

Reactors were placed in the 34°C hot room to enhance the growth of methanogens.



NOT TO SCALE

Figure 3.3. Leachate Distribution System

3.1.2. Simulated Landfill Reactors Loading

Simulated landfill reactors were filled with shredded and compacted synthetic solid waste of composition presented in Table 3.1. The purpose of using the synthetic solid waste was to assure accelerated stabilization, establish the identity and maximize the homogeneity of the refuse.

The numbers given in the Table 3.1. represent the average of typical municipal solid waste composition determined for five zones in the city of Istanbul, selected according to the different socio-economically situation and type of fuel used for heating [48].

Table 3.1. Synthetic Solid Waste Composition

COMPOSITION	PERCENTAGE (%)
Food	76
Paper	12
Plastics	4
Textiles	4
Yard Waste	3
Metal	1
Total	100

The solid waste mixture of approximately 26 kg was separated into two portions. Representative samples of 10 grams were obtained from each portion for moisture determination.

Before the solid waste loading, a nylon screen with 1 mm diameter holes was placed at the bottom of each reactor. A 1-2 cm tick layer of all purpose gravel was placed on the nylon screen. About 13 kg of solid waste was then loaded to each reactor and manually compacted. The average in-place density of solid waste in each reactor was 178 kg/m^3 [48]. A rubber gasket was placed on a PVC flange prior to placement of a PVC top lid. The reactors were sealed with silicone between the joints of PVC flange and top lid to make them gas tight. Reactors were purged with nitrogen gas to displace oxygen from the system and to directly establish the anaerobic conditions.

3.1.3. Simulated Landfill Reactors Operation

3.1.3.1. Moisture Application and Management

Preliminary analysis indicated that the solid waste had approximately 80% moisture content. To be sure that the moisture content is sufficient for waste to reach field capacity, i.e. to commence producing leachate, one liter of water was introduced to each reactor at the beginning of experiment. This day was defined as Day 0. The water application procedure was constantly repeated for 4 days until the amount of liquid introduced each day was equal to the amount of liquid collected on the next day. Some extra water additions were done on Days 8, 9, 13, and 17 to reassure that field capacity is reached. The total volume of water applied to each reactor until field capacity was attained was 10 liters. Fraction of the leachate obtained from each reactor on Day 1 (1.5 liters from the single pass reactor and approximately 0.8 L from recycle reactor) was stored in 2 L glass bottles for subsequent use and/or analysis.

The introduction of leachate to the recycle reactor and water to the single pass reactor was commenced on Day 22. Introduction of water to recycle reactor was commenced on Day 128. The application rate of water to the reactors was 500 mL/week, corresponding to an equivalent of 20 cm/year rainfall infiltration. Total amount of water added to single pass reactor during the experimental period was 28.5 L, while total amount of water added to recycle reactor was 21 L. Total amount of leachate internally recycled to recycle reactor was 138 L.

To see the effects of different moisture regimes on solid waste stabilization process, the volume of recirculated leachate and frequency of recirculation to recycle reactor were periodically changed. The maximum volume of recirculated leachate did not exceed 2 L in order to prevent flooding in the reactor. Recirculation frequency was gradually increased from one to four times per week. Taking into the consideration cost of pumping in real case examples, four times per week recirculation was determined to be the maximum appropriate recirculation frequency. As a last phase of the experiment, recirculation with leachate buffering was practiced as an attempt to enhance the activity of methanogenic population and accelerate the landfill stabilization. Total of 700 mL 1 N KOH was added in this phase. Throughout the study period, water was applied to the single pass reactor at a constant rate of 500 mL/week. The experimental study was divided into six operational stages outlined in the Table 3.2.

Stage I commenced on Day 0 and lasted until Day 22. During this stage 1 L of water was added to the reactor periodically to increase the moisture content of the waste until waste reached its field capacity.

Stage II commenced on Day 22 and lasted until Day 90. During this stage, 1 L of leachate was recirculated once per week. No water was added during this stage.

Stage III commenced on Day 90 and lasted until Day 146. During this stage, 2 L of leachate was recirculated once per week. No water was added up to Day 125 when 500 mL/week water addition commenced.

Stage IV commenced on Day 146 and lasted until Day 194. During this stage, 2 L of leachate was recirculated twice per week with weekly water addition of 500 mL.

Stage V commenced on Day 194 and lasted until Day 222. During this stage, 2 L of leachate was recirculated three times per week with weekly water addition of 500 mL.

Stage VI commenced on Day 222 and lasted until Day 249. During this stage, 2 L of leachate was recirculated four times per week with weekly water addition of 500 mL.

Stage VII commenced on Day 249 and lasted until Day 275. During this stage, leachate was buffered to neutral pH with total of 700 mL 1 N KOH prior to its recirculation. 2 L of leachate was recirculated four times per week with weekly water addition of 500 mL.

Table 3.2. Operational Stages Employed Throughout the Experimental Study to the Recycle Reactor

		VOLUME ADDED (mL)		FREQUENCY	
STAGE	DAYS	LEACHATE	WATER	RECIRCULATION	WATER ADDITION
I	0-22	-	1000	-	periodically
II	22-90	1000	-	1/week	-
III	90-146	2000	500[1]	1/week	1/week
IV	146-194	2000	500	2/week	1/week
V	194-222	2000	500	3/week	1/week
VI	222-249	2000	500	4/week	1/week
VII	249-275	2000[2]	500	4/week	1/week

[1] commenced on Day 125

[2] buffered to neutral pH

3.1.3.2. Sludge Seeding Procedure

To initiate and enhance the rate of solid waste degradation and stabilization with methane production, each reactor was seeded with 1 L of anaerobic digested sludge collected from Tekel Rakı factory in Beykoz (Istanbul). The seeding was done on Day 0, right after the placement of synthetic refuse into the reactors. The anaerobic sludge had 1.69 percent solids of which 88 percent were volatile solids.

3.2. Sampling and Analytical Methods

Leachate and gas were produced in the simulated landfill reactors every day as solid waste degradation progressed under anaerobic conditions. 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 single pass and the recycle reactors, and were analyzed for chemical oxygen demand (COD), pH, oxidation-reduction potential (ORP), ammonia nitrogen, alkalinity, and anions (chloride, sulfate, phosphate).

COD was monitored to reflect the degree of stabilization and the availability of organics in the leachate. After their collection, leachate samples were diluted with deionized water. 2.5 mL of each sample were pipeted into HACH vials containing 1.5 mL of potassium dichromate and 3.5 mL of acid digestion mixture. The vials were then placed into HACH COD reactor and digested for two hours at 150°C. After digestion samples were analyzed using a HACH Portable Water Analysis Instrumentation DR/3 Spectrophotometer. Up to Day 169, COD was monitored on a daily basis, after that, three times a week.

Measurements of the leachate pH was a simple and effective means to determine the extent to which stabilization were occurring in each reactor. A pH probe attached to WTW pH 320 pH meter was used to determine the pH of leachate samples. pH was monitored on a daily basis.

The ORP of leachate samples were determined in order to provide an indication of the oxidation-reduction conditions present in each reactor. A ORP probe attached to a ORION SA520 pH meter was used for determination of the ORP. ORP was monitored on a daily basis.

Leachate ammonia nitrogen was monitored to determine its availability as an essential nutrient. Ammonia nitrogen concentrations were determined using a Gerhardt Vapodest 12 distillation unit followed by the titration in accordance with Standard Methods 418 A - 418 D [49]. Up to Day 80 ammonia nitrogen was monitored twice a week, after that, once a week.

Orthophosphate, chloride and alkalinity were monitored according to the methods 425F (Ascorbic Acid Method), 408 A (Argentometric Method), and 403, respectively, outlined in the Standard Methods for the Examination of Water and Wastewater [49].

Sulfate is monitored using Sulfaver 4 HACH method. Pillows containing Sulfaver 4® powder were poured into 25 ml of sample and allowed 5 minutes for turbidity to develop. Sulfate concentration is known to be proportional to the developed turbidity, as determined using HACH Portable Water Analysis Instrumentation DR/3 Spectrophotometer.

The daily temperature, gas production rate, and gas composition were also observed. Inverted graduated cylinders, used for determination of gas production rate, were filled with an acidic solution to avoid the dissolution of methane in the liquid [47]. The displacement of the acidic solution in the gas collection cylinders was recorded on a daily basis as a daily gas production. When enough gas was produced to fill the gas collection cylinder, it was vented by opening the gas venting hose clamp. Gas composition was measured by collecting 10 mL gas samples through the rubber septum at the top of each reactor into 10 mL glass airtight bottles using airtight syringe. Gas composition, measured as percentage by volume, was determined for carbon dioxide and methane. Collected samples were injected into a gas chromatograph HP 5890 equipped with 8 ft HEYSEP Q 80/100 19093A packed column, using nitrogen as a carrier gas. Injection port and detector were operated at $150^{O}C$ and $160^{O}C$, respectively. The oven temperature was programmed to start at $70^{O}C$ and was gradually increased $5^{O}C$ per minute until final temperature of $150^{O}C$

was reached. Pure carbon dioxide and methane standards were used to calibrate gas chromatograph and obtain calibration curves.

Details about frequency and method of analyses are given in Table 3.3.

Table 3.3. Analysis Method and Frequency of Simulated Landfill Leachate and Gas Parameters

MEASUREMENT	PROCEDURE	FREQUENCY
pH	EPA 600/4-79-020, Method 120.1	every day
ORP	Standard Methods for Water and Wastewater Examination # 2580	every day
COD	Standard Methods for Water and Wastewater Examination #5220 - D	every day/ three times a week
CH_4, CO_2	Gas Chromatography	once a week
Ammonia Nitrogen	Standard Methods for Water and Wastewater Examination, Method 418 A- 418 D, Acidimetric Method	twice a week /once a week
Orthophosphate	Standard Methods for Water and Wastewater Examination, Method 425 F, Ascorbic Acid Method	every 2 weeks
Chloride	Standard Methods for Water and Wastewater Examination, Section 408.A, Argentometric Method	once a week
Alkalinity	Standard Methods for Water and Wastewater Examination, Section 403	once a week
SO_4^{-2}	HACH Sulfaver 4 Method	once a week

4. RESULTS AND DISCUSSION

4.1. Preliminary Analysis

4.1.1. Solid Waste Analysis

In order to determine the moisture content of the solid waste, two representative samples of approximately 10 grams were obtained from the waste matrix. The samples were placed in a dish, weighted and dried in the 105°C oven for 24 hours. After the samples were re-weighted, the moisture content of waste matrix in the single pass and recycle reactors was calculated to be 78 percent and 75 percent, respectively.

4.1.2. Anaerobic Digested Sludge Analysis

In order to determine percentages of solid and volatile solids in the seeding sludge, two representative samples of 50 ml were analyzed. The samples were poured in the dishes, weighted, evaporated and dried at 105 ^{O}C. After the samples were re-weighted, the percentage of solid in the sludge was computed. The samples were ignited at 550^{O}C for 1 hour to determine the volatile solids percentage of the seeding sludge. The anaerobic digested sludge was determined to contain 1.69 percent solids of which 88 percent was volatile solids.

4.2. Reactor Experiment

4.2.1. Water Balance

After the reactors were loaded and sealed water and gas tight, tap water was added until field capacity of the waste matrix was reached. From the moisture analysis of the solid waste, initial water content was determined to be 6.0 L and 5.7 L in the single pass and recycle reactor, respectively. Total of 10 L of tap water was added to both reactors until field capacity was reached. Of that, single pass and recycle reactors retained 1.0 L and 1.05 L, respectively. Total moisture content available in the column at the beginning of the experiment was estimated to be 7.0 L and 6.75 L for the single pass and recycle column, respectively.

Water additions were continued to both reactors according to the management strategy applied through the seven operational stages outlined in the Section 3.1.3.1. Throughout the study, total of 28.5 L and 21.0 L of tap water was added to the single pass reactor and recycle reactor, respectively (Figure 4.1. and Figure 4.2.). Additionally, 700 mL of 1 N KOH was added to the recycle reactor throughout the Phase VII to increase the pH to 7.0.

Leachate from the single pass reactor was removed for sampling purposes and wasting, while leachate from the recycle column was removed for sampling purposes only. By assuming the average amount of leachate removed daily was 5 mL, a total amount of leachate from each reactor that was wasted for experimental purposes throughout the study was found to be 0.9 L. Additionally, 1.5 L and 0.8 L of leachate from the single pass and recycle reactor, respectively, were removed on Day 1 for subsequent analysis.

Lecahate was also removed from each column as a result of moisture losses during gas production [15]. However, the calculated values were negligible, being 6.27×10^{-7} L and 2.46×10^{-6} L for single pass and recycle reactors, respectively. Procedure used for determination of losses due to gas production is outlined in the Appendix A.

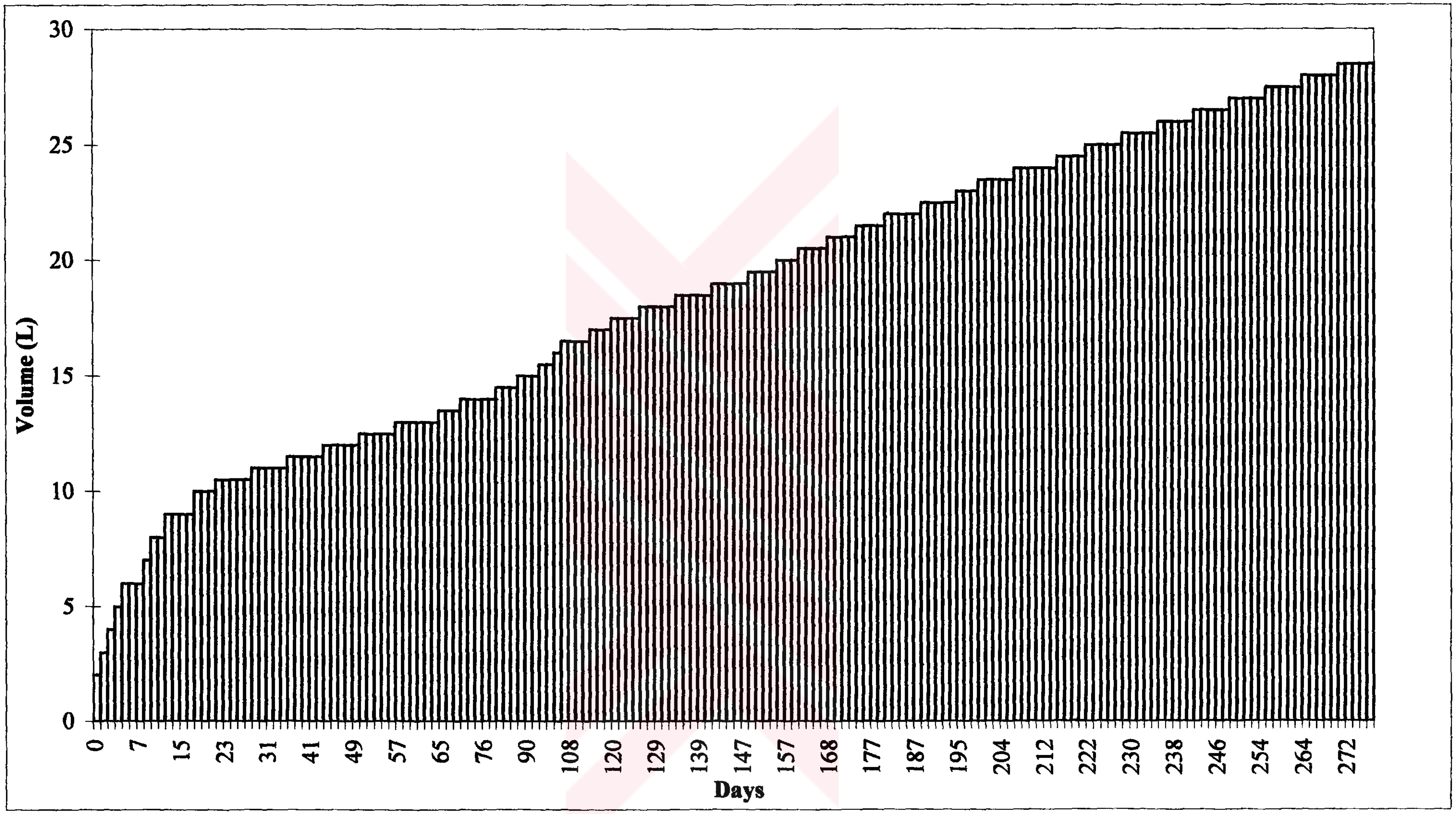


Figure 4.1. Cumulative Volume of Liquid Added to the Single Pass Reactor

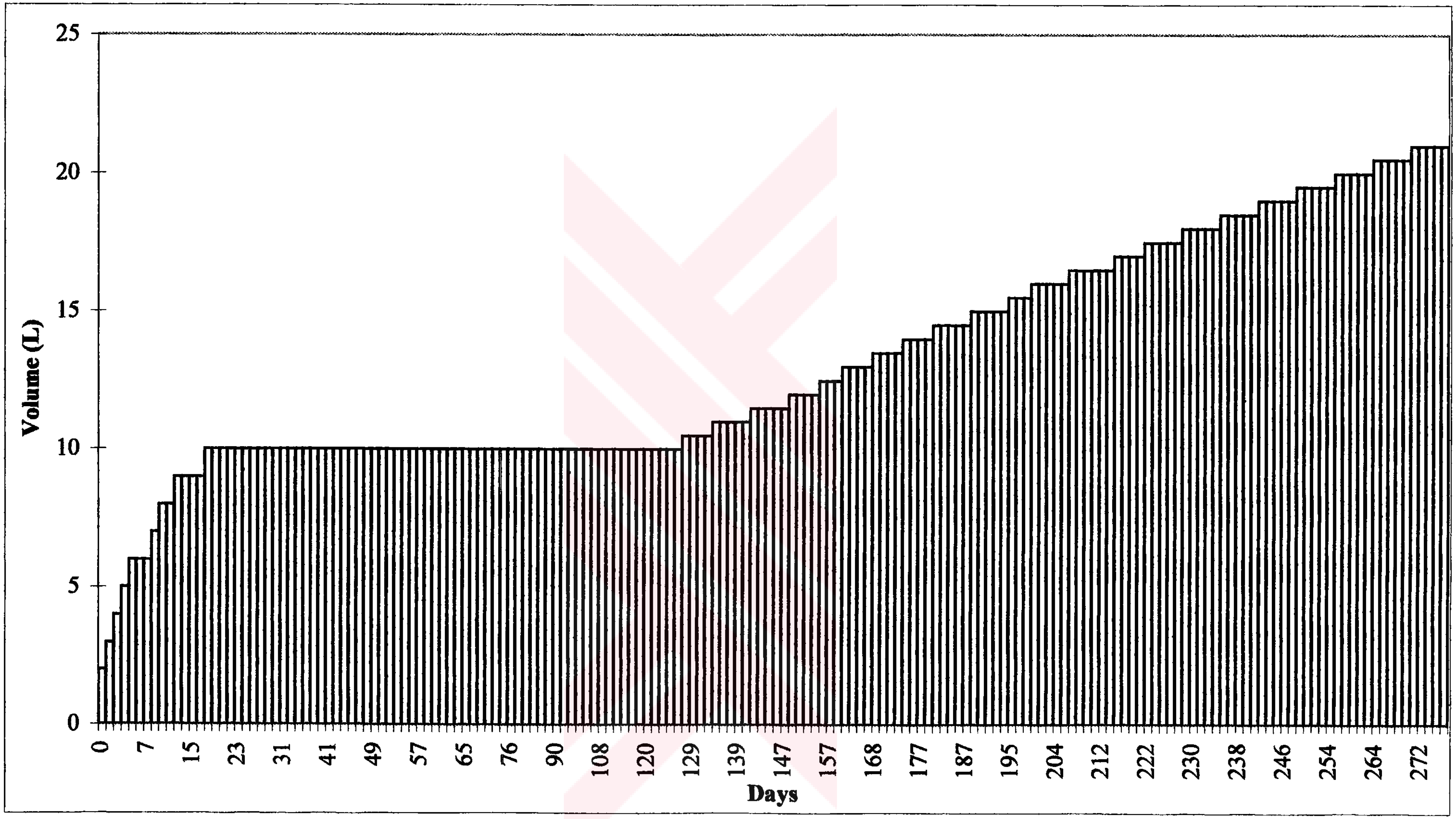


Figure 4.2. Cumulative Volume of Liquid Added to the Recycle Reactor

At the end of the experimental study, amount of water collected in the leachate storage tank was 24.8 L and 19.9 L for single pass and recycle reactor, respectively (Figure 4.3. and Figure 4.4.). Total of 138 L of leachate was internally recycled to the recycle reactor.

The information presented above may be tabulated as follows:

	WATER (L)			
	INITIAL	ADDED	COLLECTED	WASTED
Single Pass	6.0	28.5	24.8	2.4
Recycle	5.7	21.7	19.9	1.7

Using the water balance approach;

$$\Delta W = W_{initial} + W_{added} + W_{collected} - W_{wasted} \qquad [14]$$

where;

ΔW = change in the amount of water stored in solid waste (L);

$W_{initial}$ = initial moisture content of solid waste (L),

W_{added} = amount of water added to the reactor (L),

$W_{collected}$ = amount of water (leachate) collected in the collection tank (L),

W_{wasted} = amount of water wasted for experimental analysis (L).

ΔW for single pass reactor = $6 + 28.5 - 24.8 - 2.4 = 7.3$

ΔW for recycle reactor = $5.7 + 21.7 - 19.9 - 1.7 = 5.8$

If assumed that no other losses occurred during the study period, the result obtained represent the available water in the single pass and recycle columns at the end of the experiment. The difference between initial and final moisture content of the single pass and recycle column may be attributed to the losses due to the evaporation during recirculation and inaccurate estimation of losses due to sampling. These values are going to be used later for the COD mass calculations.

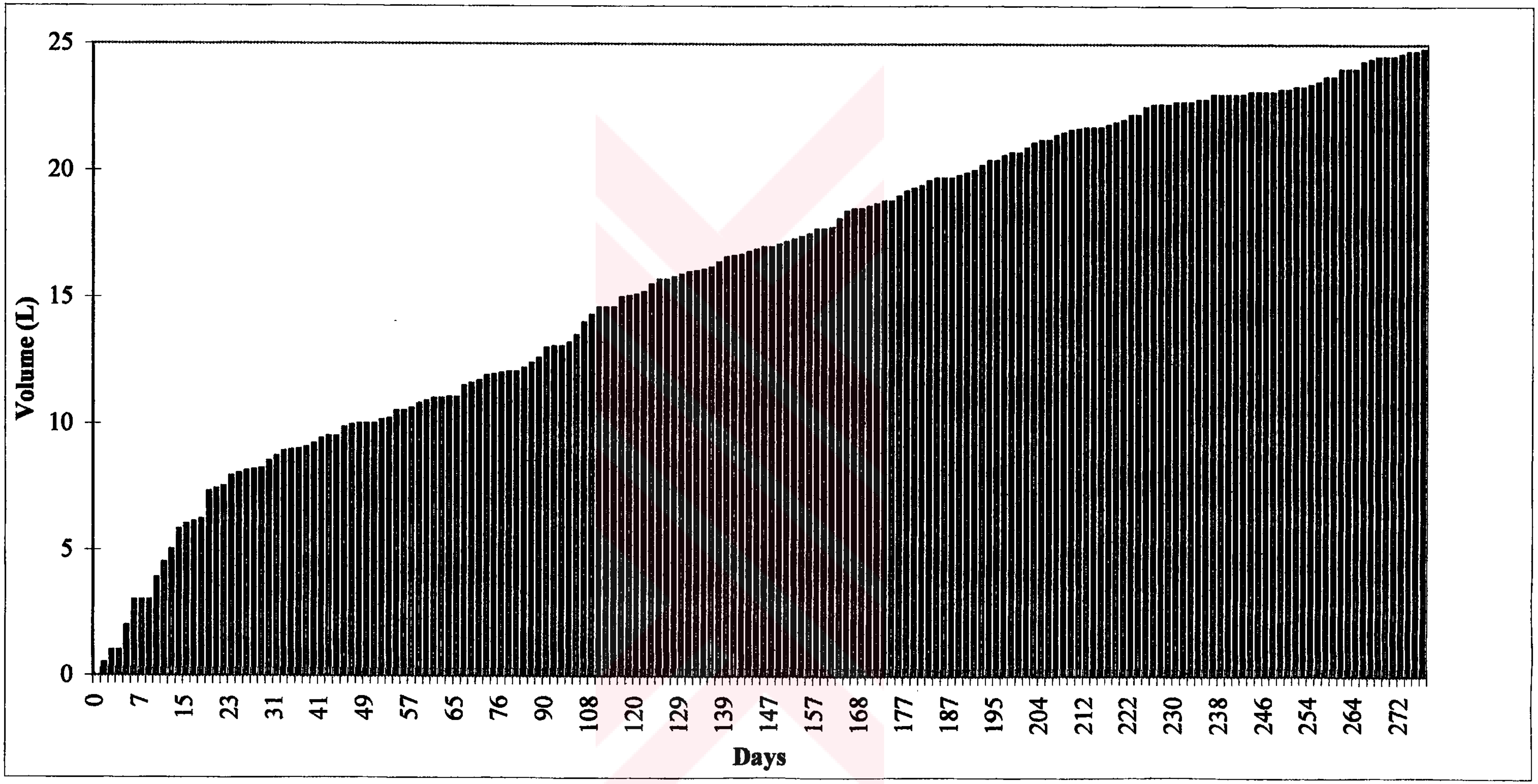


Figure 4.3. Cumulative Volume of Liquid Collected from the Single Pass Reactor

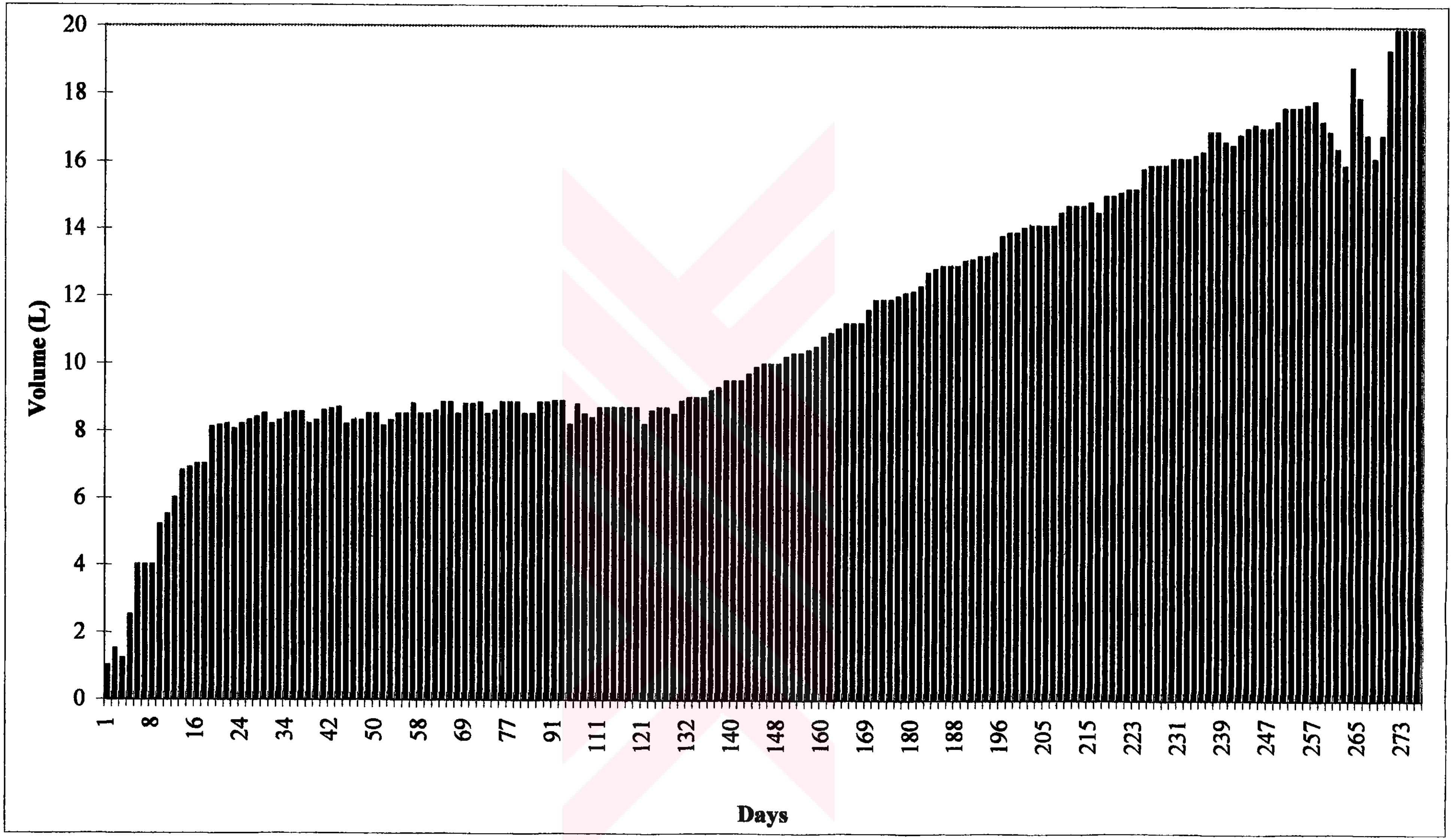


Figure 4.4. Cumulative Volume of Liquid Collected from the Recycle Reactor

4.2.2. Leachate Analysis

The main environmental factors affecting the rate of stabilization of the landfill are pH, ORP, chemical oxygen demand, nutrients (ammonia and phosphorus), ionic strength (sulfate, chloride) and alkalinity. In this study, these parameters were monitored to detect and describe the presence, intensity and duration of each phase of landfill stabilization.

4.2.2.1. pH

In landfill anaerobic system pH may be the most important indicative parameter. The chemical and biological reactions occurring in a landfill are all function of pH. The pH of the system depends upon the relationship between the volatile acids and alkalinity in the leachate and carbon dioxide content in the gas produced during the stabilization process. During the acid formation phase of landfill stabilization, excessive production of volatile fatty acids and their accumulation cause pH values to be lower. Although the methanogenesis process is know to occur in acidic as well as alkaline environments [10], low pH is considered to be more inhibitory to methanogens than fermentative bacteria. As the landfill stabilization enters the methane fermentation phase, pH values increases to more neutral values due to conversion of volatile fatty acids and hydrogen to methane and carbon dioxide.

The measured leachate pH values from both reactors are presented in the Figure 4.5. Initially high value of pH during the first 10 days of Phase I decreases as the initial adjustment phase is completed and anaerobic decomposition of waste proceeded. Release of volatile fatty acids throughout the operational Phase II results in depression of pH as low as 5.2 on Day 52. The pH values of both recycle and single pass reactors showed the similar decreasing trend through the first five stages of experiment, having the average value of 5.5. However, after the Day 222 of Phase VI, when the leachate recirculation frequency was increased to four times per week, slight increase in pH of leachate from recycle reactor was observed. The increase from 5.5 on Day 221 to nearly 6.0 on Day 247 is the result of conversion of volatile organic acids to methane and carbon dioxide, and consequently, increased stabilization of recycle reactor.

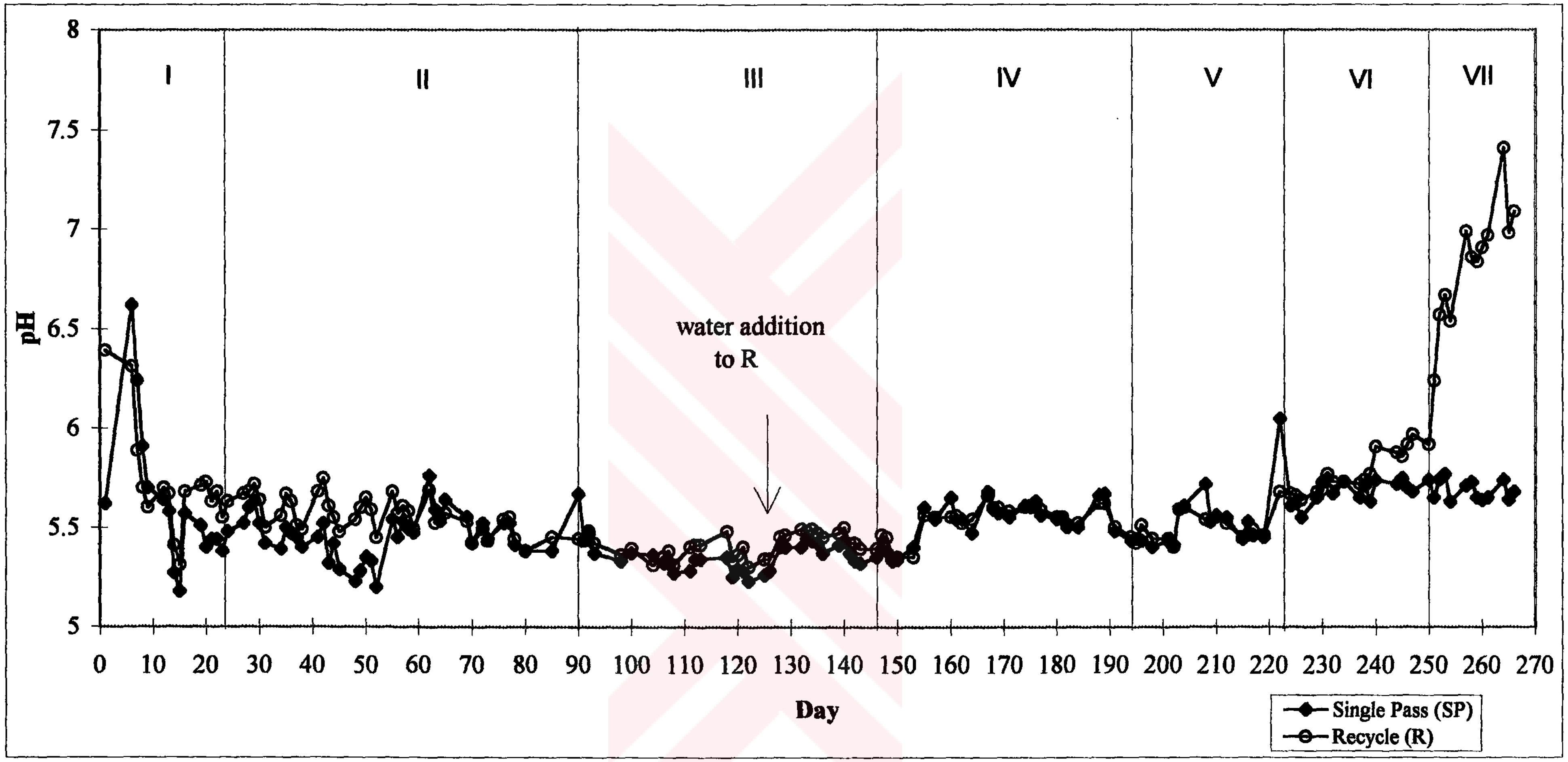


Figure 4.5. pH of Leachate from the Single Pass and Recycle Reactors

However, the pH of the recycle column was still not favorable for the development of active methanogenic population. As reported by Farquhar and Rovers [9], the optimum pH for methanogens is near 7.0. In order to speed up the stabilization process and establish the active methanogenic population, an attempt was made to increase the pH of leachate from the recycle reactor from 6.0 to 7.0 by adding the 1 N KOH, and recycle the mixture back to the recycle reactor four times per week. This resulted in the increase in pH of the recycle reactor from 5.92 on Day 250 to 7.3 on Day 257. In contrast to the recycle reactor, pH of the single pass reactor remained constant at the pH of about 5.5.

4.2.2.2. ORP

ORP is physical-chemical parameter indicative of the oxidation-reduction potential of the system. During the initial adjustment and transitional phase of waste stabilization ORP values are positive due to the oxygen presence in the system. Once the oxygen is depleted, anaerobic conditions dominate and ORP value became negative. As ORP value is lower, the environment within the landfill is more reducing which favors both anaerobic fermentation and sulfate reduction.

The measured ORP values for both reactors are presented in the Figure 4.6. After the solid waste is placed in the reactors, system was purged with the nitrogen gas. This sudden displacement of oxygen from the system resulted in the very low values of ORP. However, the ORP values have started to increase to about -50 mV in single pass leachate and -70 mV in recycle leachate on Day 48, where the solid waste has reached its field capacity and real environmental conditions have been established. The increase in recirculated leachate volume from 1 L to 2 L during the Phase III did not effect the ORP values. However, the ORP values of recycle reactor began to be more negative on Day 150 (Phase IV) as a direct result of increased leachate recirculation frequency from one to two times per week. Further slight decrease of the ORP value continued throughout the Phase V and VI where leachate recirculation frequency was changed from two to three, and from three to four times per week, respectively. Progressive decline of ORP continued as a waste stabilization process proceeded being enhanced by changing leachate recirculation

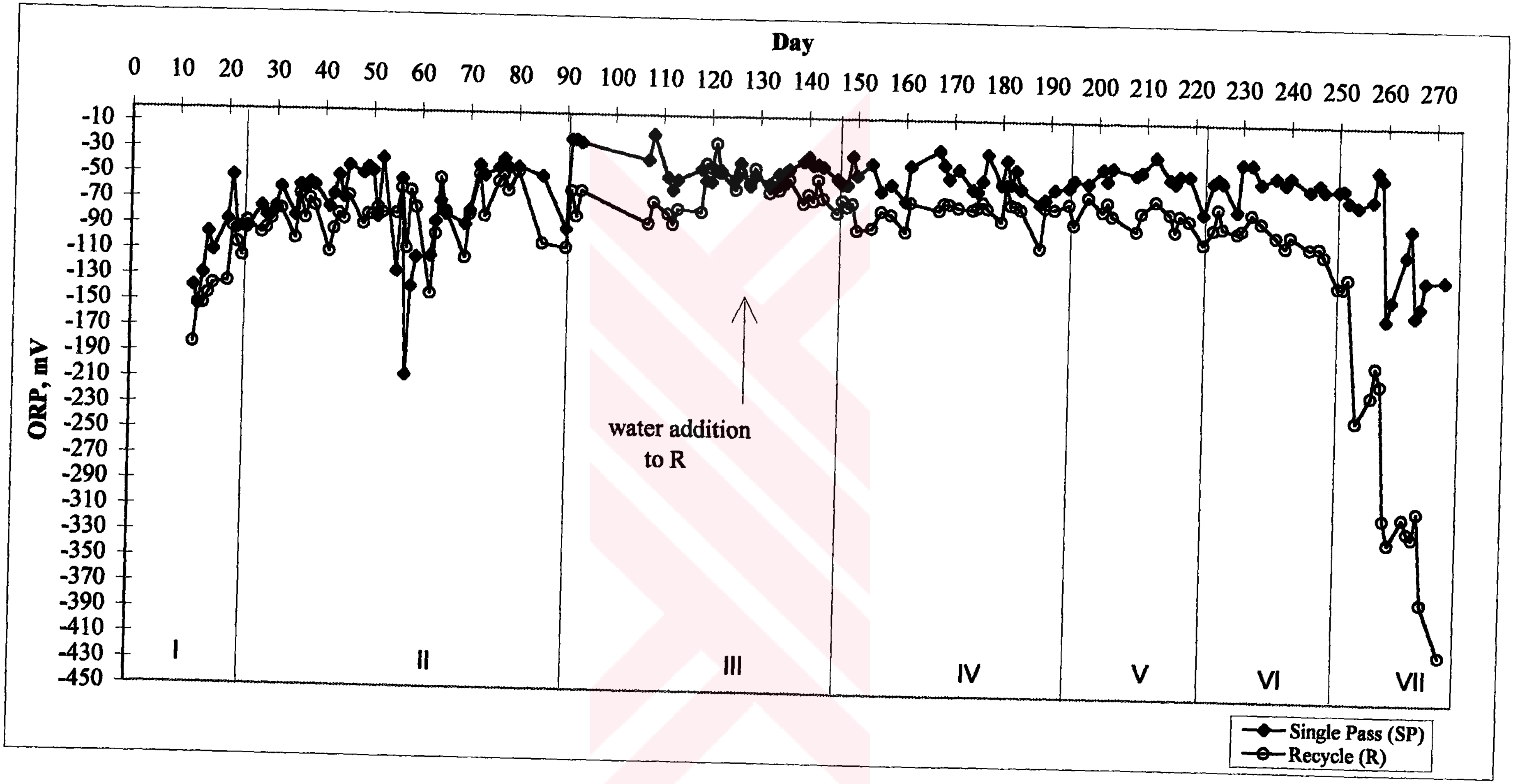


Figure 4.6. ORP of Leachate from the Single Pass and Recycle Reactors

frequency, while the ORP values of the single pass reactor was remained to be less negative during the experimental period. ORP values dramatically decreased after Day 250 and throughout the Phase VII as a direct consequence of recycling buffered leachate. Leachate buffered to pH 7.5 helped establishing environmental conditions favored by methanogens, increasing reducing conditions inside the reactors and lowering the ORP from -125mV on Day 272 to -412 mV on Day 268.

4.2.2.3. Chemical Oxygen Demand (COD)

Chemical oxygen demand is a chemical parameter indicative of the organic strength of leachate in terms of the amounts of oxygen needed to obtain oxidation of the chemically oxidizable fractions contained within the waste. COD concentrations for recycle and the single pass reactors are given in Figure 4.7.

Initial concentration of COD in both reactors was found to be similar indicating the uniformity in waste composition in both reactors. In Phase I, as the result of rapid release of organics from the solid waste into leachate and dissolution of the organic acids, COD concentrations for the single pass and recycle reactor increased from 5000 mg/L to 45,000 mg/L and 39,000 mg/L, respectively. Decomposition process in the recycle reactor continues throughout the Phase II and increases to 46,000 mg/L on Day 64. This decomposition delay with respect to single pass reactor resulted from the different operating moisture regimes, and may be related to difference in moisture available in two reactors. The increase in the volume of recirculated leachate from 1 L to 2 L did not seem to effect the COD concentration that remains constant with daily fluctuations throughout the beginning of the Phase III. However, after the Day 125, COD concentration in the recycle reactor started to decrease as a consequence of water addition. Addition of extra 500 mL of water increased moisture content of the waste to the levels optimal for the decomposition of the organic matter. This was confirmed by the increased methane concentrations that followed the COD decrease after the Day 125. The change in recirculation frequency through Phases IV to VI resulted in faster decomposition of the solid waste, reflected by decrease in the COD concentration accompanied with rapid

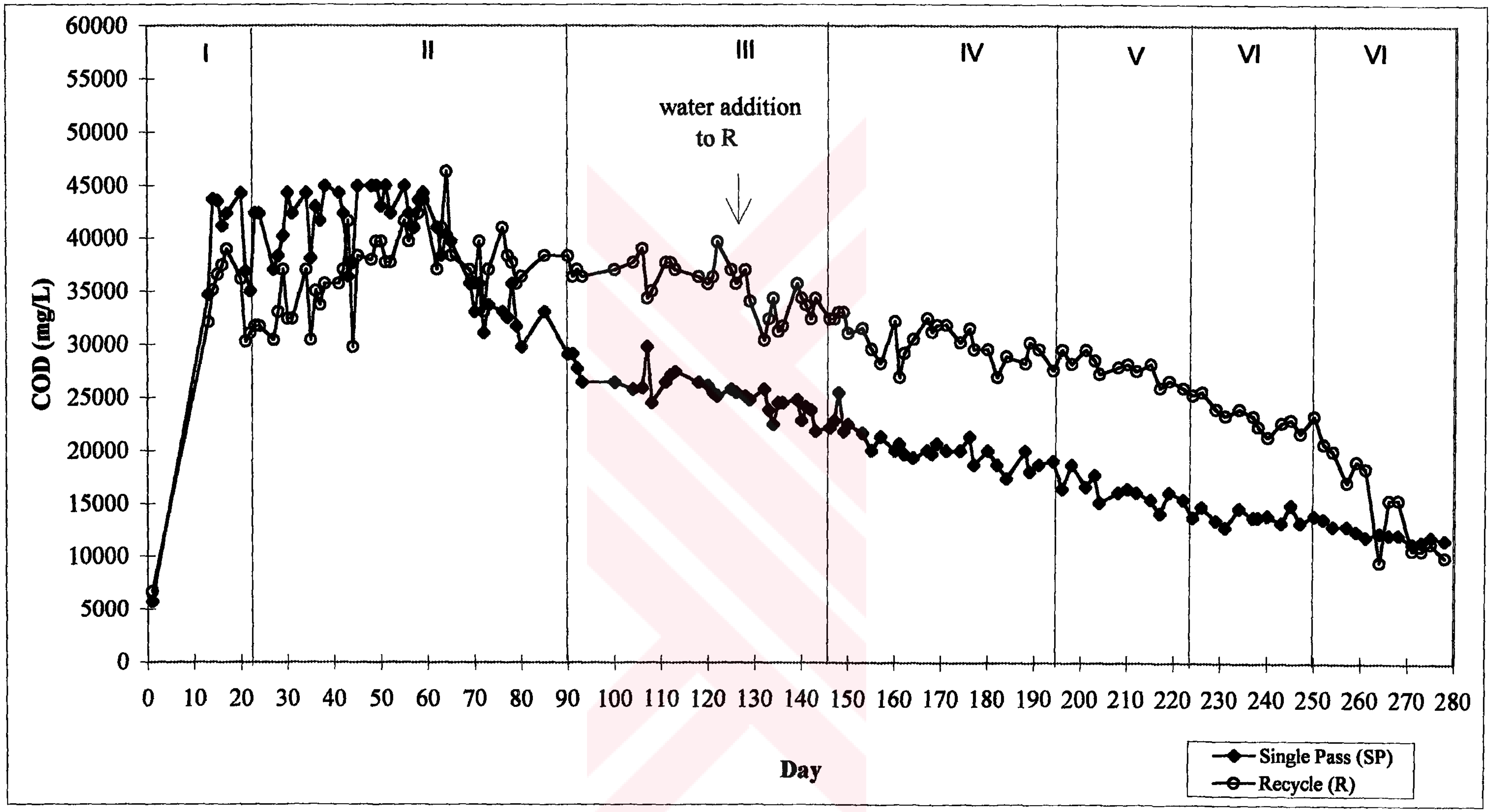


Figure 4.7. COD Concentration in Leachate from the Single Pass and Recycle Reactors

increase in methane concentration. The highest methane concentrations were obtained during the Phase VI when recirculation frequency was changed from three to four times per week. The decrease in COD concentration from 26,000 mg/L on Day 222 to 21,500 mg/L on Day 240 was accompanied with the decrease in methane concentration from 47 percent on Day 218 to 51 percent on Day 234.

Buffering the leachate prior its recirculation even more accelerated waste decomposition. In Phase VII, COD concentrations in the recycle reactor decreased from 23,300 mg/L on Day 250 to 9500 on Day 264. However, it was observed that recycle column held more moisture than in the previous phases, retaining whole amount of recycled leachate on days when recirculation was done (from Monday through Thursday). This may resulted in flooding conditions in the recycle reactor. As a consequence, accumulation of volatile acids was observed as confirmed with slight decrease in pH values on these days. On the other hand, during the non-recirculation days (from Friday to Sunday), the leachate previously retained was leaching out and microbial activity was accelerating. This resulted in higher utilization of volatile organic acids, as confirmed by increase in pH, and decrease in COD concentrations. Therefore, COD concentrations measured during the week were much higher than concentrations measured after the weekend. Moisture and acid accumulation negatively affected methanogens by retarding their activity and lowering methane concentrations.

In contrast to the recycle reactor, organic strength reduction in leachate from the single pass reactor was not the result of the waste stabilization process. The decrease from 45,000 mg/L to 13,500 mg/L was the result of dilution and washout mechanism that was dominated in the single pass reactor. This was validated by observing the behavior of other parameters affecting the waste stabilization. While COD concentration showed decreasing trend, methane concentration remained low, and ORP and pH values well below the ultimate for the stabilization of waste. Furthermore, the color of the leachate was light yellow in contrast to recycle leachate that was brown-yellow, confirming the dilution.

The results obtained related to the changes in COD concentrations have showed that the simulated landfill operated with leachate neutralization and recirculation have the greater ability for waste stabilization then the one with single pass leaching.

4.2.2.4.Ammonia Nitrogen

Adequate amounts of nutrients are essential for supporting the growth and maintenance of microbial population, as well as the efficient operation of anaerobic waste stabilization process. Nitrogen is needed for the production of protein, enzymes, ribonucleic acid (RNA), and deoxyribonucleic acid (RNA). Ammonia nitrogen is produced from the decomposition of organic material containing nitrogen and is utilized by anaerobic bacteria. Availability of the nitrogen for the microbial utilization was measured as ammonia nitrogen and expressed as mg/L of nitrogen. Ammonia nitrogen concentrations for the single pass and the recycle reactors are given in Figure 4.8.

Initial concentration of ammonia nitrogen in both reactors was found to be similar indicating the uniformity in waste composition in both reactors. Increasing trend of ammonia nitrogen in both reactors during the Phase I is the result of its rapid release as the initial decomposition of organic material containing nitrogen proceeds. Ammonia nitrogen increased from initially concentrations of 0 mg/L NH_3-N and 115 mg/L NH_3-N, to maximum 747 mg/L NH_3-N and 976 mg/L NH_3-N, for the single pass and recycle reactor, respectively. Determined concentrations were lower then the inhibitory value reported to be 1500 mg/L [15].

While the washout mechanism in the single pass reactor caused ammonia nitrogen concentration to decrease, recirculation practice in recycle reactor reintroduced ammonia back into the system, keeping its value nearly constant. The increase in ammonia concentration in the recycle reactor was due to the enhancement of the stabilization process. This observation was confirmed by Onay and Pohland [32]. Changes in recirculation frequency during the Phases IV, V and VI resulted in slight decrease in the ammonia nitrogen concentration. The increased microbial activity confirmed by decrease in COD and increase in methane concentrations, has resulted in greater biological assimilation of ammonia nitrogen by microbial population within the recycle reactor.

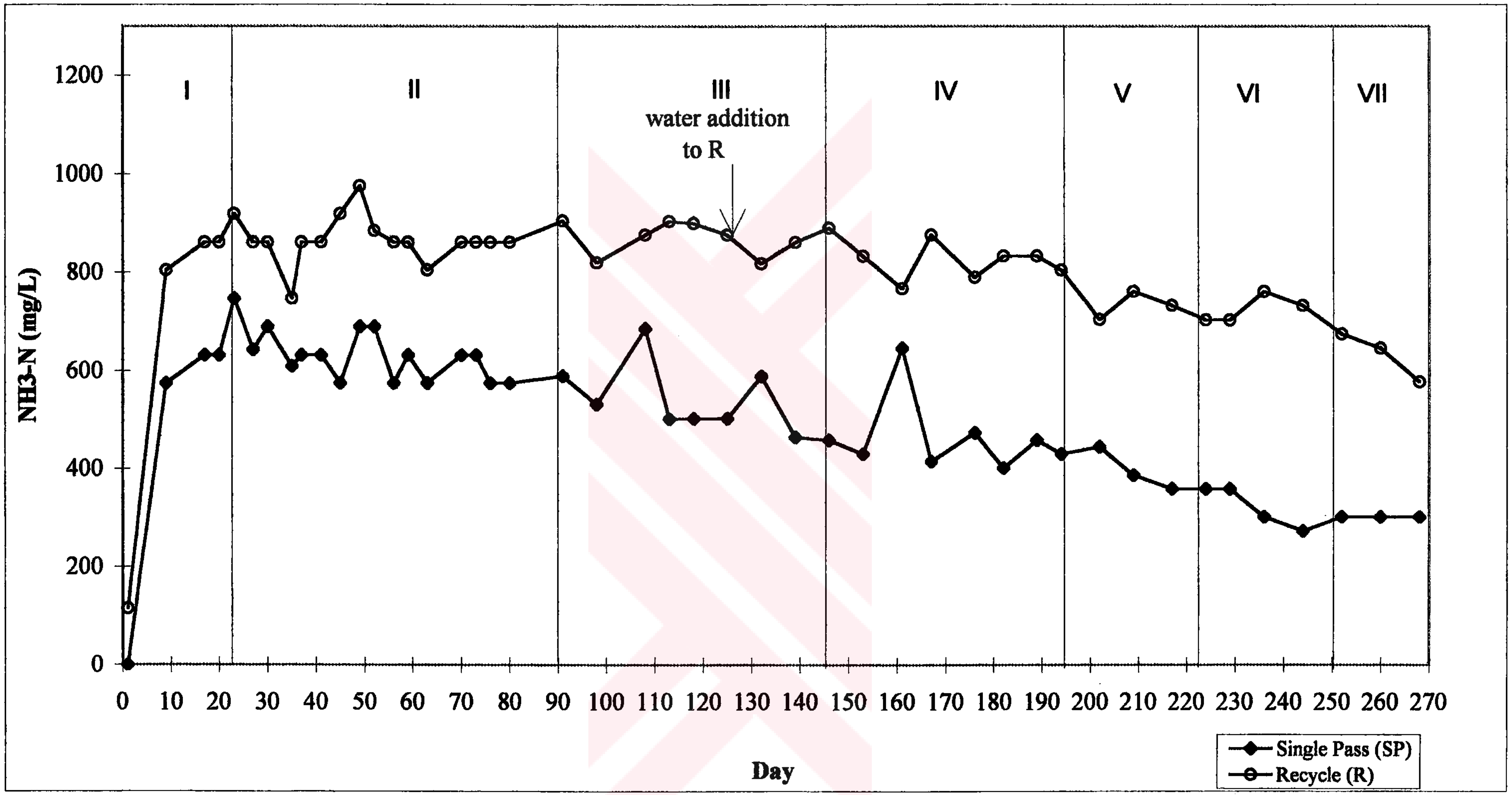


Figure 4.8. Ammonia-Nitrogen in Leachate from the Single Pass and Recycle Reactors

At the end of the experiment period, the ammonia nitrogen value in single pass reactor was 270 mg/L. Observed value is greater then minimum required 100 mg/L [19], therefore considered to be sufficient for active bacterial populations.

4.2.2.5.Orthophosphate

Another nutrient necessary for growth and performance of the microbial population is phosphorus. Phosphorus is used to synthesize energy-storage compounds (adenosine triphosphate-ATP) as well as RNA and DNA. Availability of the phosphorus for the microbial utilization was measured as orthophosphate and expressed as mg/L of phosphorus. Orthophosphate concentrations for the single pass and the recycle reactors are given in Figure 4.9.

Initial concentration of orthophosphate in both reactors was found to be similar indicating the uniformity in waste composition in both reactors. Rapid decomposition of organic material resulted in increasing trend of orthophosphate concentration during the Phase I. The concentrations reach 280 mg/L PO_4-P and 260 mg/L PO_4-P for the single pass and the recycle reactors, respectively. Although initially orthophosphate concentrations for single pass and recycle reactors were the same, slight increase in the single pass reactor concentration after Day 13 was due to the different operational moisture regimes. The concentrations of orthophosphate in both reactors balanced after the water addition to recycle reactor commenced on Day 125. After the Day 34, decreasing trend in the values from both reactors was observed due to the increased activity of microorganisms. Toward the end of experiment, decrease in the orthophosphate concentration of single pass reactor and recycle reactors was observed. Decrease in orthophosphate concentration of the single pass reactor was the result of washout mechanism, while the decrease in concentration of recycle reactor is the result of greater phosphorus biological utilization. Still, the determined values of 61 mg/L and 19 mg/L for single pass and recycle reactor, respectively, at the end of the experimental study were considered sufficient for microbial activity since they satisfy nutrient requirement of the system reported to be COD:N:P = 100:0.44:0.08 [7].

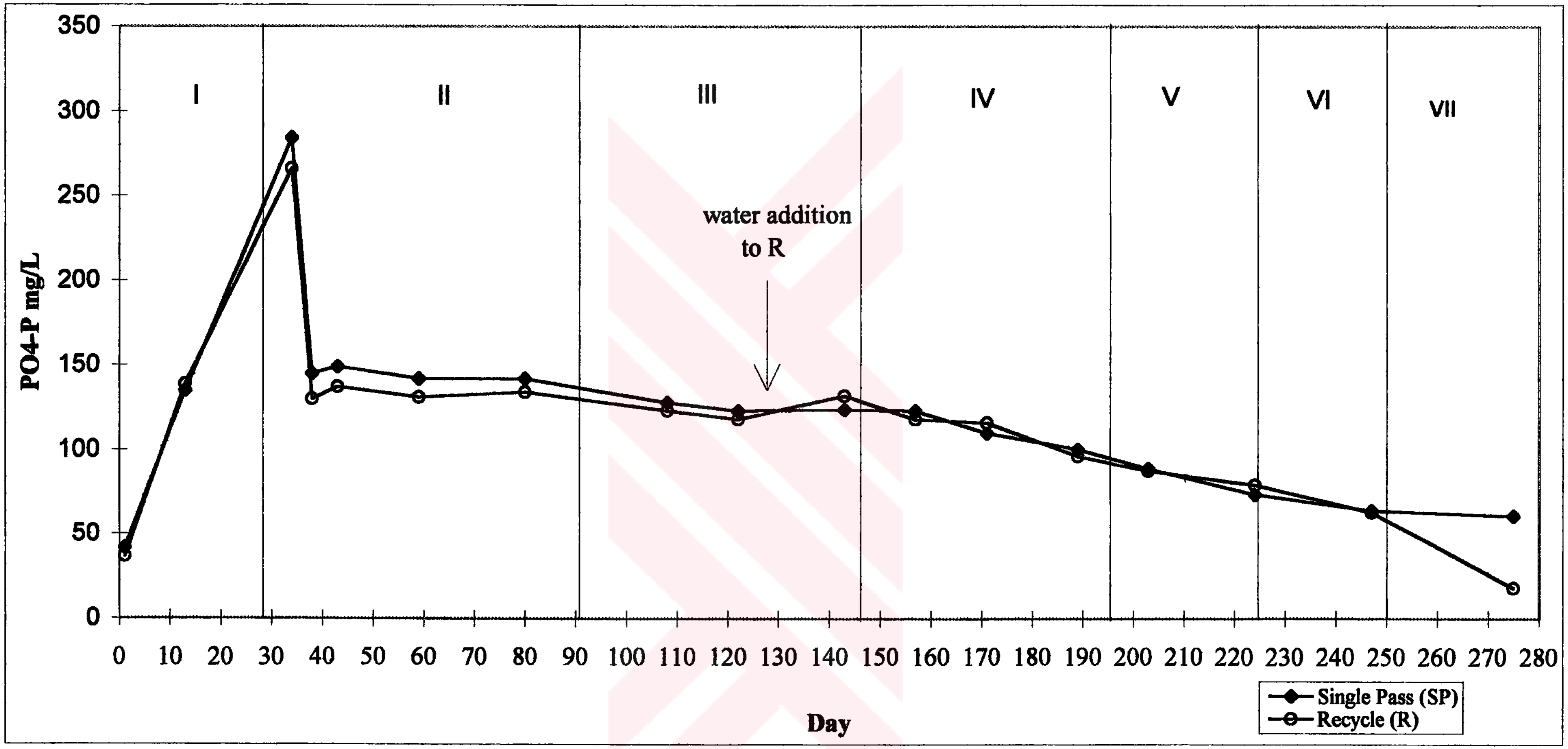


Figure 4.9. Orthophosphate in Leachate from the Single Pass and Recycle Reactors

4.2.2.6.Alkalinity

Alkalinity represents a capability of system to buffer effects of volatile and other acids which tend to depress the pH below desired level. The alkalinity of the system is reflected by the association of cations and anions present in the system including volatile acids, ammonium, calcium and magnesium, and sodium [31]. The presence of a buffer capacity in the system is very important for the continuity of the biological stabilization processes. The measured alkalinity concentrations for the single pass and the recycle reactors are given in the Figure 4.10.

Initially high alkalinity concentrations in both reactors followed the decomposition of the waste and release of the volatile organic acids. Higher alkalinity concentration in the leachate from the recycle reactor, when compared to a single pass reactor, was reflected by high ammonia concentrations available in the system. Apart from the weekly fluctuation, decrease in alkalinity concentration throughout the study period was observed. Leachate recycle enhanced the utilization of organic portion of the waste, therefore resulting in decrease of volatile organic acids and slight increase of the pH. As a consequence, alkalinity concentration of the recycle reactor leachate decreased from 6300 mg/L as $CaCO_3$ on Day 55 to 3000 mg/L as $CaCO_3$ at the end of the experimental study.

The decrease in alkalinity from the single pass leachate, from 5500 mg/L as $CaCO_3$ on Day 63 to nearly 1500 mg/L at the end of the experimental study, was primarily due to washout of cations and anions responsible for the formation of the alkalinity. Although the determined value is less than 2000 mg/L, reported to be desirable for well established anaerobic system [19], no fluctuations in pH confirm that the remaining alkalinity was enough to buffer the possible inhibitory effects of the volatile acids.

4.2.2.7.Chloride

In order to observe the effects of leachate management strategies upon priority pollutant behavior and fate, leachate chloride concentration was measured as a tracer not

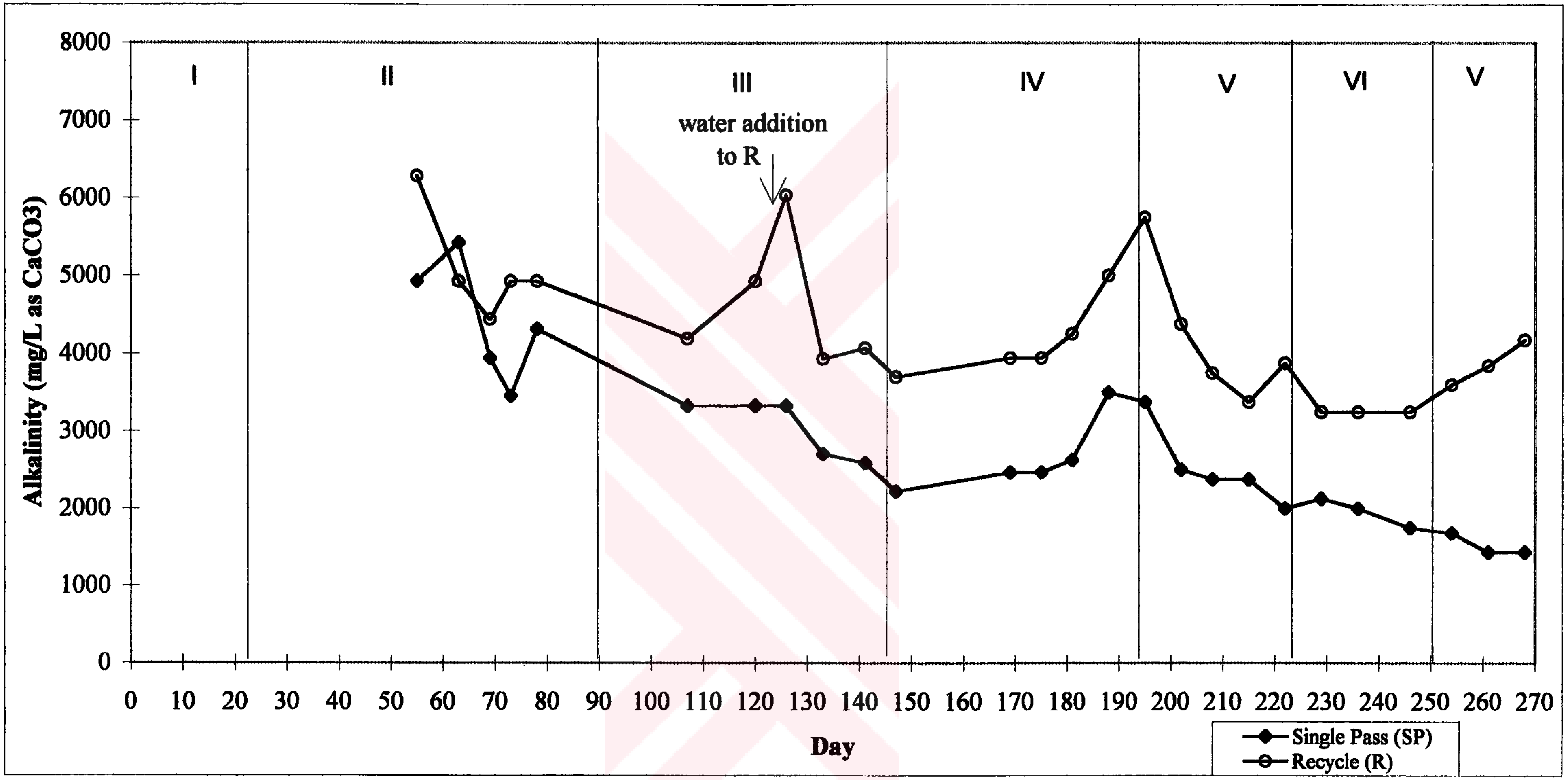


Figure 4.10. Alkalinity in Leachate from the Single Pass and Recycle Reactors

affected by any biological conversion. Chloride concentrations for single pass and the recycle reactors are given in the Figure 4.11.

Throughout the Phases II and III, leachate chloride concentration in the recycle rector remained constant after the initial period of leaching and mobilization. Increase in the leachate recirculation frequency in Phases IV, V, and VI resulted in increased number of flushes through the waste matrix. As a consequence, chloride concentration decreased from nearly 1000 mg/L on Day 155 to 550 mg/L on Day 261. This observation confirms the presence of minor dilution effect in the recycle column.

In contrast, leachate chloride concentration in the single pass reactor dramatically decreased during the study period. Decrease from 1000 mg/L on Day 17 to 10 mg/L on Day 268 confirm the existence of washout mechanism in the single pass column and explain the decrease in other leachate indicator parameters studied during experimental period.

4.2.2.8. Sulfate

Monitoring the sulfate concentration in the anaerobic system is of great importance. The extent to which the sulfate is reduced to sulfide is important to control the sulfide toxicity to anaerobic systems and indicates the presence of suitable reducing environment. Sulfate concentrations for the single pass and the recycle reactor are presented in the Figure 4.12.

Up to Day 254, no sulfate in the leachate from the recycle reactor was expected to be converted to sulfide as a result of inadequate reducing conditions confirmed by high ORP values, greater than -200. However, slight decrease in sulfate concentration was observed as a result of dilution effect. After Day 254, reduction in the sulfate concentration may be contributed to the reduction to sulfide since ORP values decreased to -325 on Day 261. Highly reducing conditions in the Phase VII resulted in total conversion of sulfate to sulfide, determined to be absent at the end of experiment. However, this could not be confirmed due to the difficulties of measurement sulfide in leachate.

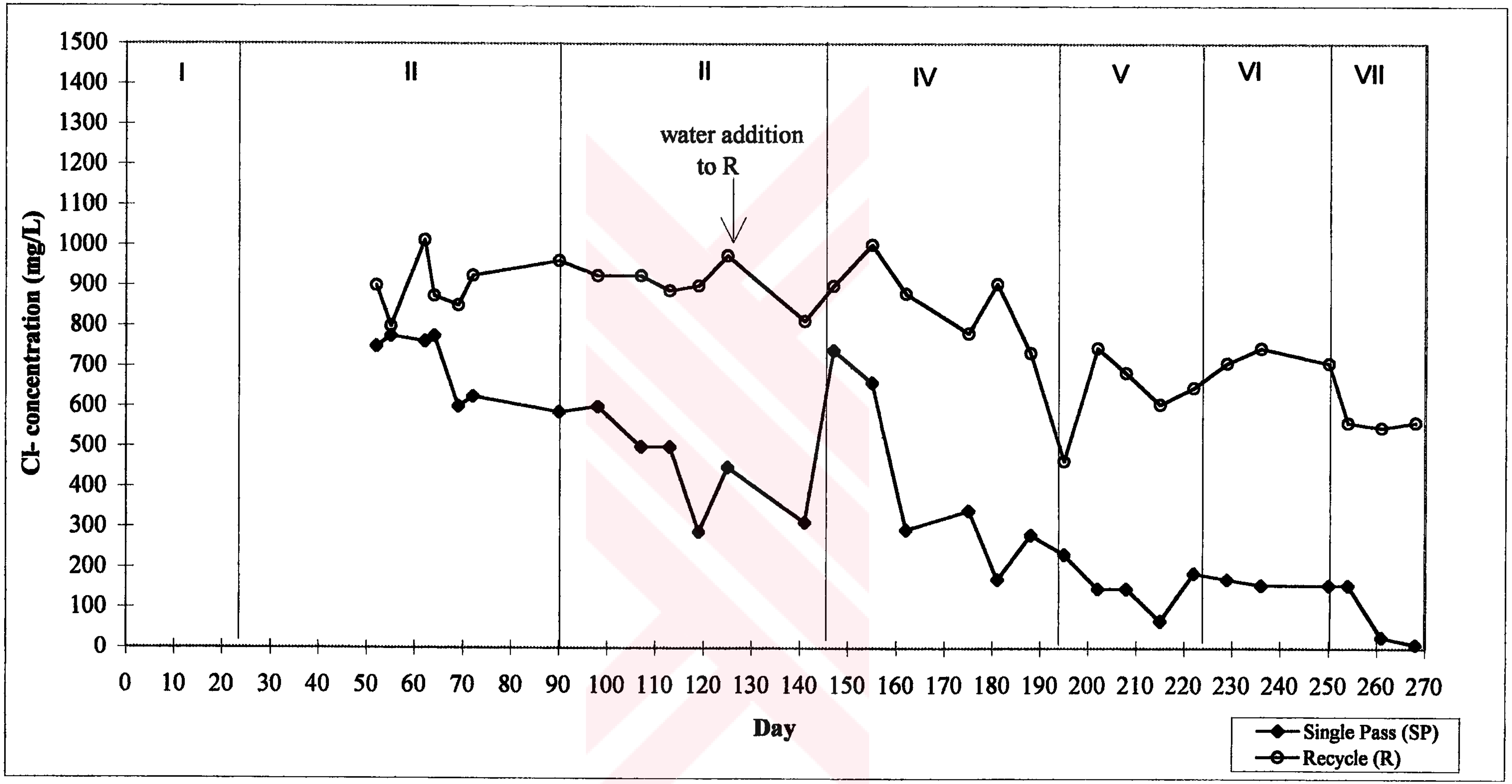


Figure 4.11. Chloride in Leachate from the Single Pass and Recycle Reactors

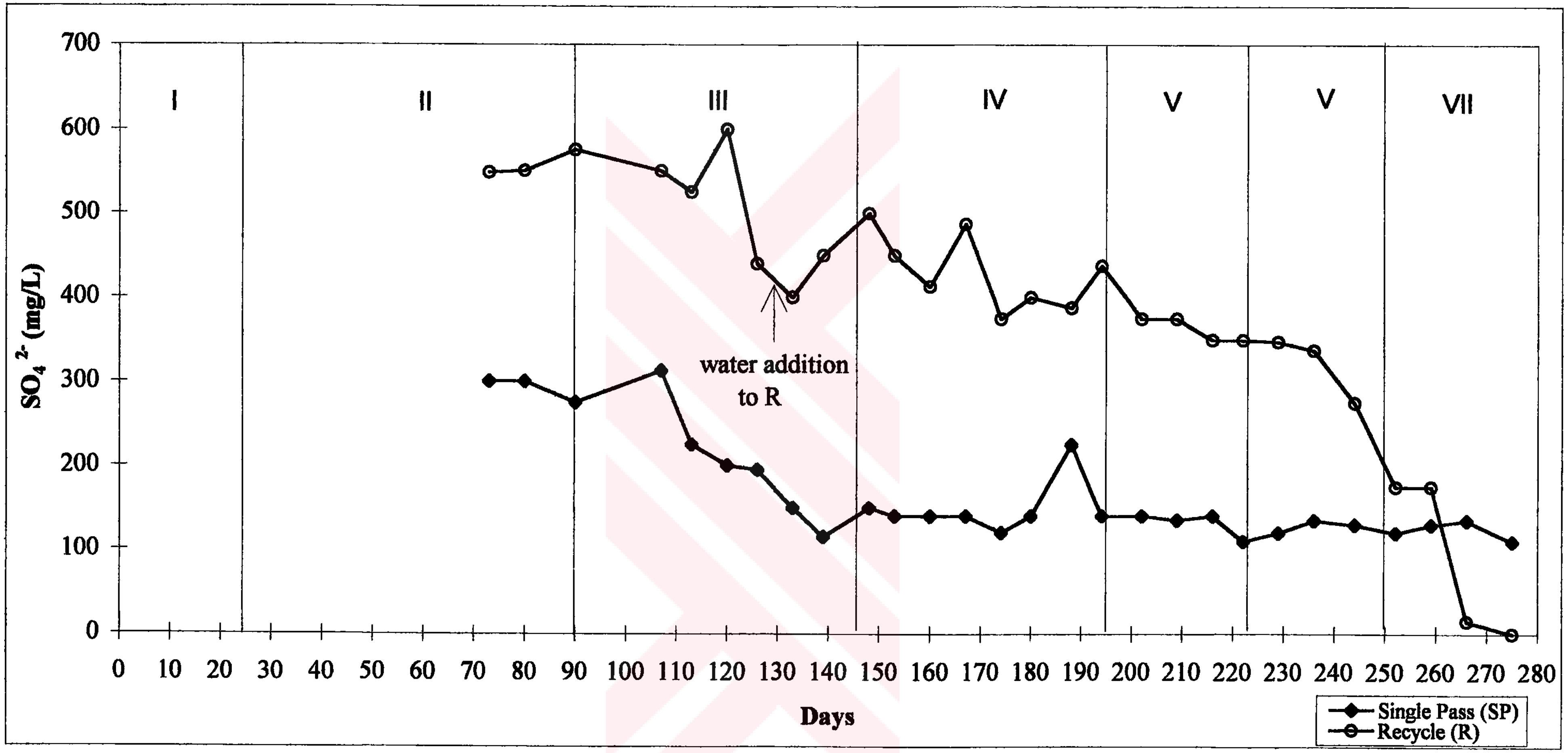


Figure 4.12. Sulfate in Leachate from the Single Pass and Recycle Reactors

Since reducing conditions in the single pass column were also insufficient to bring about conversion of sulfate to sulfide, sulfate removal in single pass column was mainly result of the washout.

4.2.3. Gas Analysis

Gas volume and quality are the main indicators of the progression of landfill stabilization process. Methane and carbon dioxide are the major products of anaerobic conversion of waste. Change in their composition reflects the biological activity within the landfill. Differences in the gas production and composition best describe the effect of different types of leachate management strategies employed upon the landfills.

4.2.3.1.Gas Production

Cumulative gas volumes produced in the single pass and recycle reactors are given in the Figure 4.13. Daily gas volumes produced in the single pass and recycle reactors are given in the Figure 4.14.

Daily gas production and, therefore, cumulative gas production for recycle reactor were extremely affected by the insufficient capacity of the gas collection unit. Daily gas production was determined by measuring the displacement of the liquid in the cylinders during the period of 24 hours. However, if the capacity of cylinders was exceeded, actual daily gas production could not be determined and the reading would be equal to the maximum capacity of cylinders. As a consequence, many of recorded values do not represent the actual daily gas production, and the cumulative gas volumes are apparently lower than it should be. On the other hand, insufficient isolation of the single pass column resulted in one-way gas diffusion from the reactor, resulting in very low daily gas production readings.

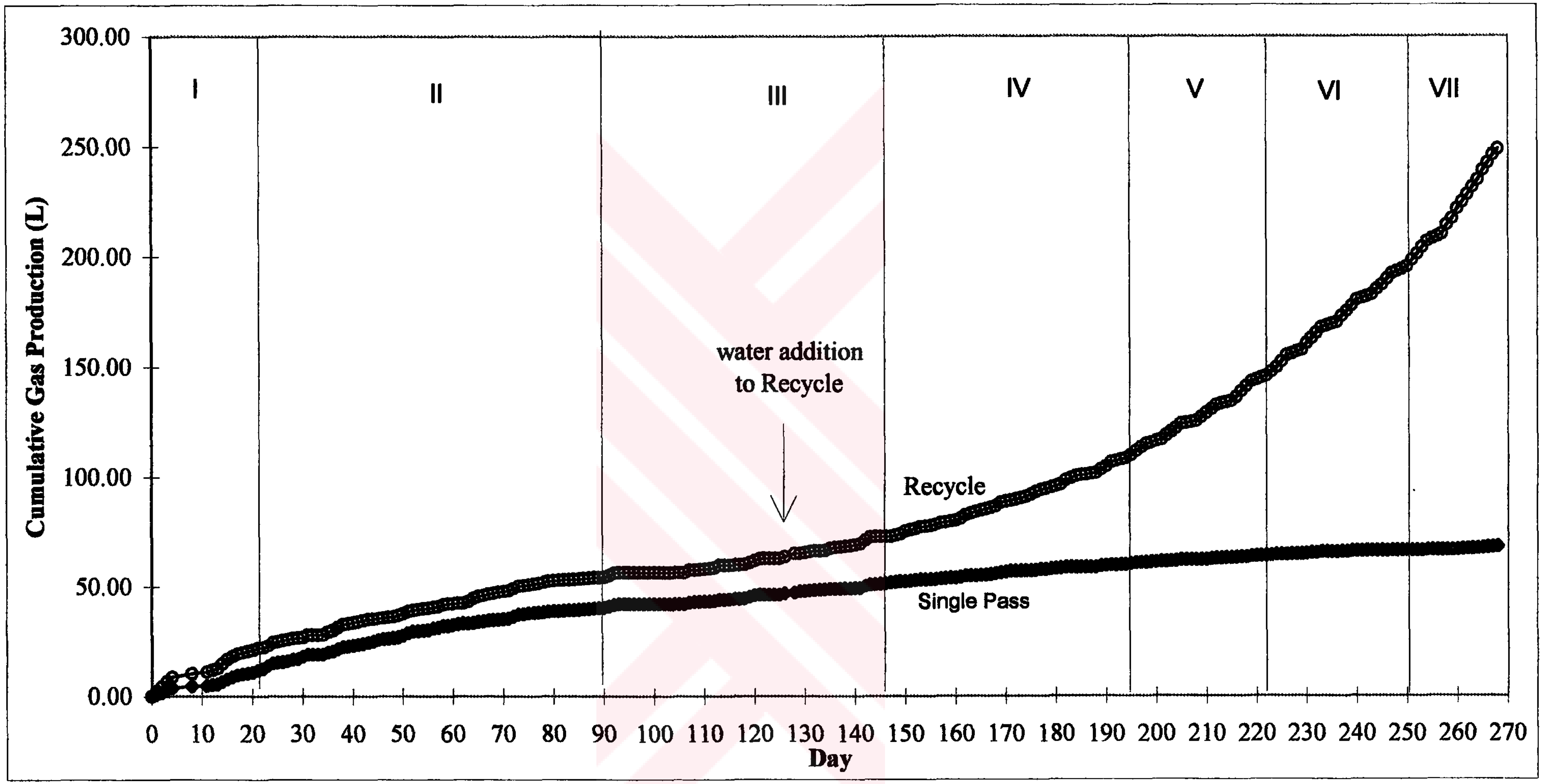


Figure 4.13. Cumulative Gas Production for Single Pass and Recycle Reactors

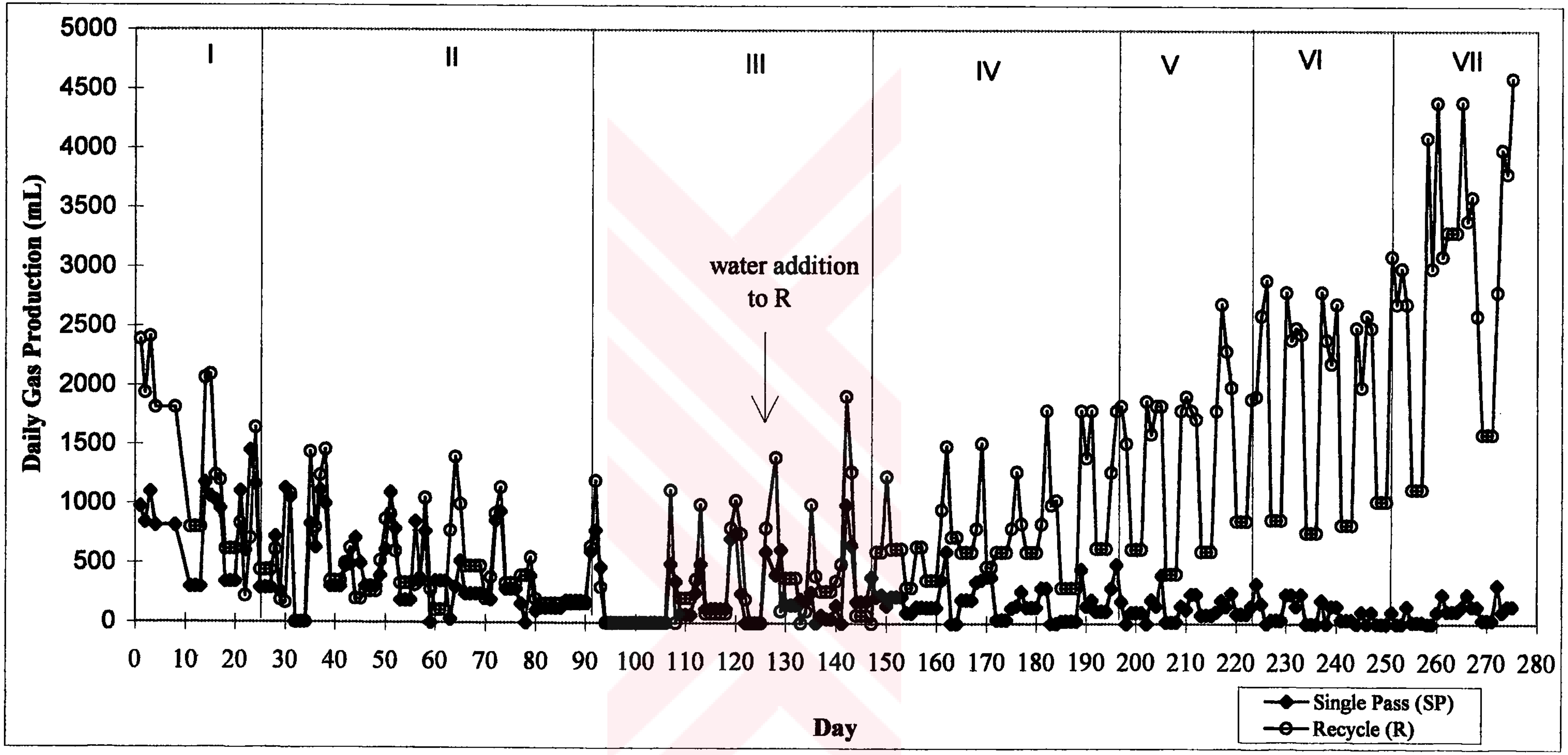


Figure 4.14. Daily Gas Production for the Single Pass and Recycle Reactors

Although results are not accurate, they can be used for qualitative characterization of reactors performance related to the microbial activity within the reactors. Dispute all these problems, from the Figure 4.13, it is obvious that the total gas produced in the recycle column was much more greater than that in the single pass column. While recycle reactor produced 269 L single pass reactor produced 70 L of gas. Leachate recycle intensified the microbial activity by reintroducing the volatile organic acids, homogenizing the environment and allowing better contact between bacteria and substrate. As a result, conversion of acids and stabilization of waste was enhanced, followed by the increase in the gas volume produced. On the other hand, necessary substrates were washout from the single pass column and conversion process continued to progress very slowly.

The increase in the volume of leachate recycled from 1L to 2L in Phase III, did not effect daily gas production. However, water addition on Day 125 resulted in slight increase in moisture content of the waste, slowly increasing microbial activity, and therefore, slightly increasing the daily gas production. Significant increase of daily gas production was observed with increase in leachate recirculation frequency from one to two times per week in Phase IV, with tremendous increase in gas production when leachate recirculation frequency increased from two to three times per week and form three to four times per week in Phases V and VI. Increased gas production is directly related to the higher degree of stabilization in recycle column and may be directly attributed to the leachate recirculation strategy employed. Leachate recirculation reintroduced substrate and necessary nutrients that would otherwise be removed from the system. Increased contact opportunity between microorganisms and substrate enhanced microbial activity and, therefore, accelerated the waste decomposition to produce final gaseous products.

Buffering of leachate prior to its recirculation in Phase VII resulted in establishing environmental conditions favored by methanogens. Reintroduction of the nutrients and substrate, together with sufficient moisture and optimum pH, accelerated the waste degradation and further increased the gas production. Gas production reached its peak during this phase.

The single pass reactor exhibited a rather unpredictable pattern of gas production. The highest volume of gas produced was 1000 mg/L on Day 142, and with the acid conditions becoming more intense, the average gas production was not exceeding 400 mg/L. One of the additional reasons for apparently low gas production was insufficient isolation of the column. There was a small leakage somewhere from the reactor, allowing diffusion of gas from the reactor and not into the reactor. Negative ORP values ranging from -40 mV to -150 mV confirmed one-way diffusion. The low gas production volumes were directly related to the washout of the substrate and essential nutrients, thus limiting the microbial activity and the waste stabilization.

4.2.3.2.Gas Composition

Methane and carbon dioxide are the principal gases produced during the decomposition of organic fraction of waste. Change in the concentration of methane and carbon dioxide reflect the rate of biological activity and organic material conversion. Differences in gas composition may be used for evaluation of effects of type of leachate management strategy employed. The gas compositions for the single pass and the recycle reactors are given in the Figure 4.15 and Figure 4.16, respectively.

Due to the lack of Gas Chromatography with thermal conductivity detector (TCD) in the Institute of Environmental Sciences laboratory, gas samples were taken to Istanbul Technical University. As a consequence of poor sampling and storage technique it was difficult to obtain the samples without introducing the air. Although results are not accurate and can not be used to determine the quantity of gas constituents, they can be used for qualitative characterization and they are sufficient to reflect relative activity within the reactors.

As shown in the Figure 4.16 n leachate volume from 1 L to 2 L during the Phase III did not affect the methane concentration in the recycle reactor. The increase in the leachate recirculation frequency from one to two times per week during the Phase IV resulted in the slight increase in the methane and carbon dioxide concentrations in recycle reactor. Increase in the methane concentration indicating that the methanogenic bacterial population has established and started to be more active. Further increase in leachate recirculation frequency, through Phases V and VI, produced dramatic changes in methane

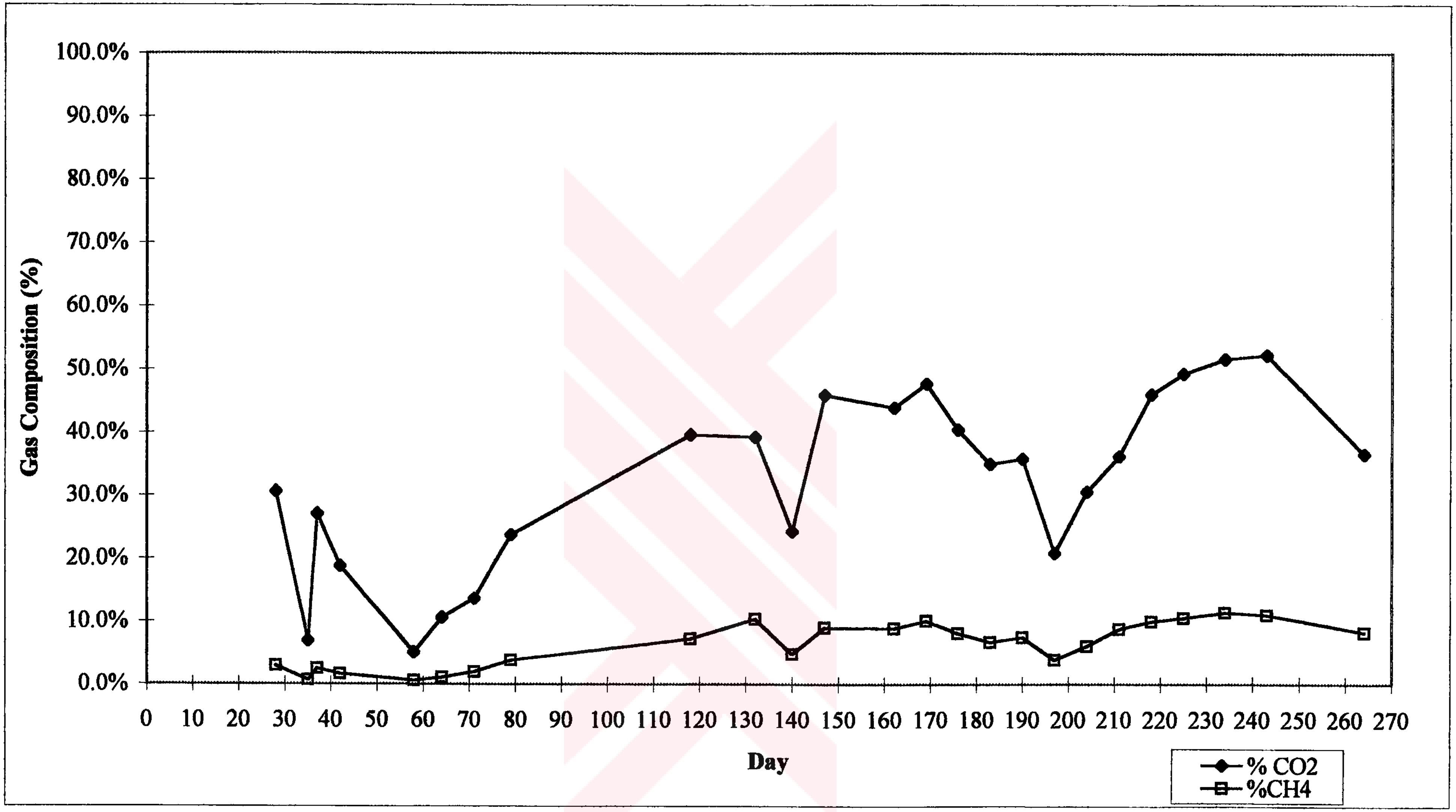


Figure 4.15. Gas Composition for the Single Pass Reactor

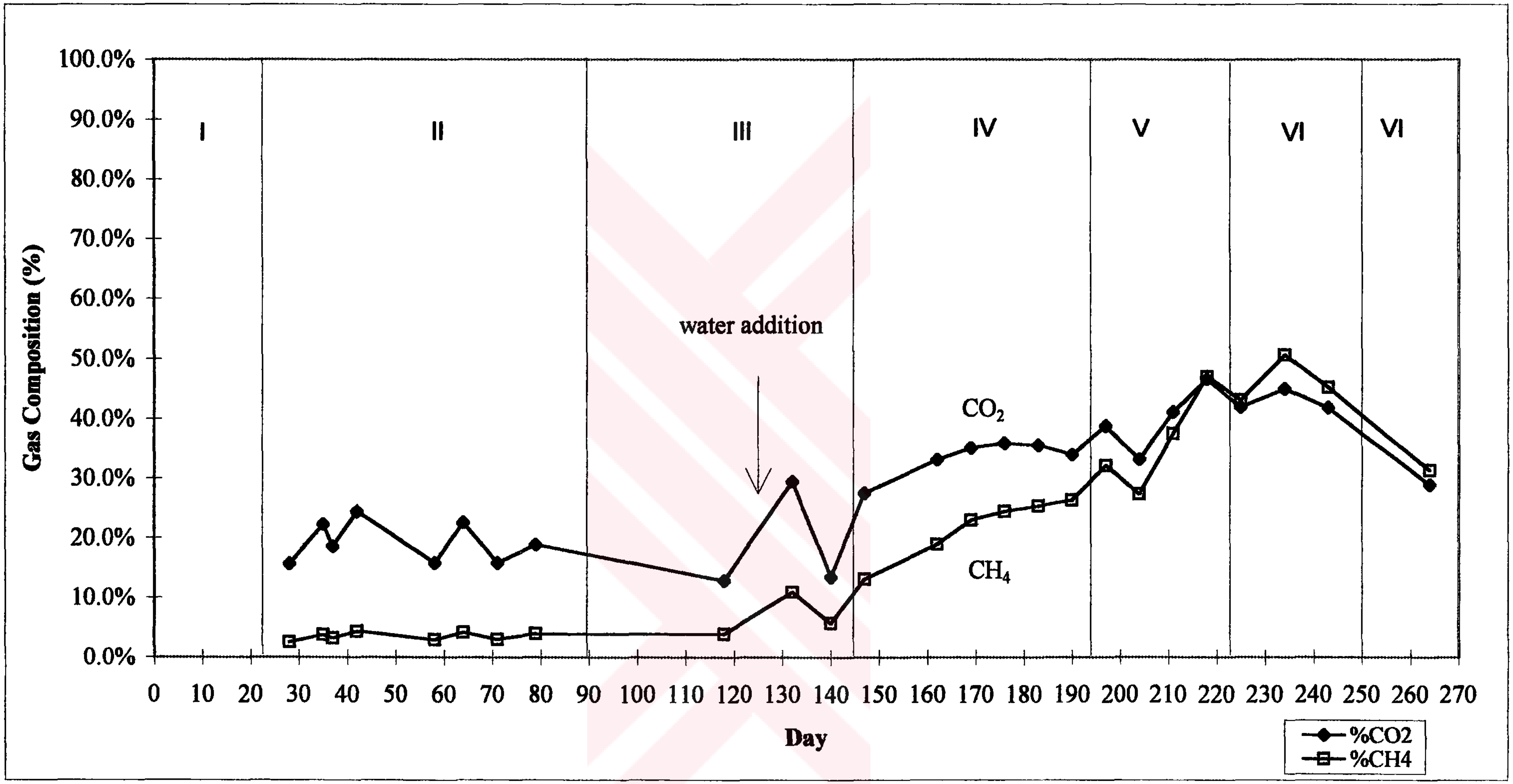


Figure 4.16. Gas Composition for the Recycle Reactor

concentration. That was the proof that the increase in recirculation frequency has positive effect on methanogenic population, enhancing their growth and activity through establishing moist environment. Due to the technical problems with Gas Chromatography, only one gas analysis was done during the Phase VII. Accumulation of moisture and organic acids on recirculation days, slowed down the activity of methanogens, thus decreasing methane and carbon dioxide concentrations from 51 percent and 45 percent on Day 234 to 31 percent and 29 percent on Day 264, respectively.

The single pass reactor exhibited a rather steady pattern of methane production with gradual increase in carbon dioxide concentration. The average methane concentration observed was 10 percent throughout the study. Low methane concentration is the evidence of washout resulting in the inability of the system to develop active methanogenic population and enhance waste stabilization.

Cumulative methane and carbon dioxide productions for the single pass and recycle reactors are given in the Figure 4.17 and Figure 4.18, respectively. Although the results are inaccurate as a direct consequence of inaccurate cumulative gas readings explained in previous section, they can be used as a useful indicator of reactors behavior. Figures clearly indicate that cumulative methane and carbon dioxide production was much higher in the recycle reactor than in the single pass reactor. While cumulative volume of methane produced in recycle reactor was 77 L, in single pass reactor only 3.2 L of methane was produced. At the same time, in recycle reactor 85 L of carbon dioxide was produced, while in single pass reactor only 18.5 L. The enormous differences in cumulative gas productions are a result of increased activity of recycle reactor when compared to single pass reactor, as a direct consequence of leachate recycle management strategy, creating a more homogeneous and moist environment.

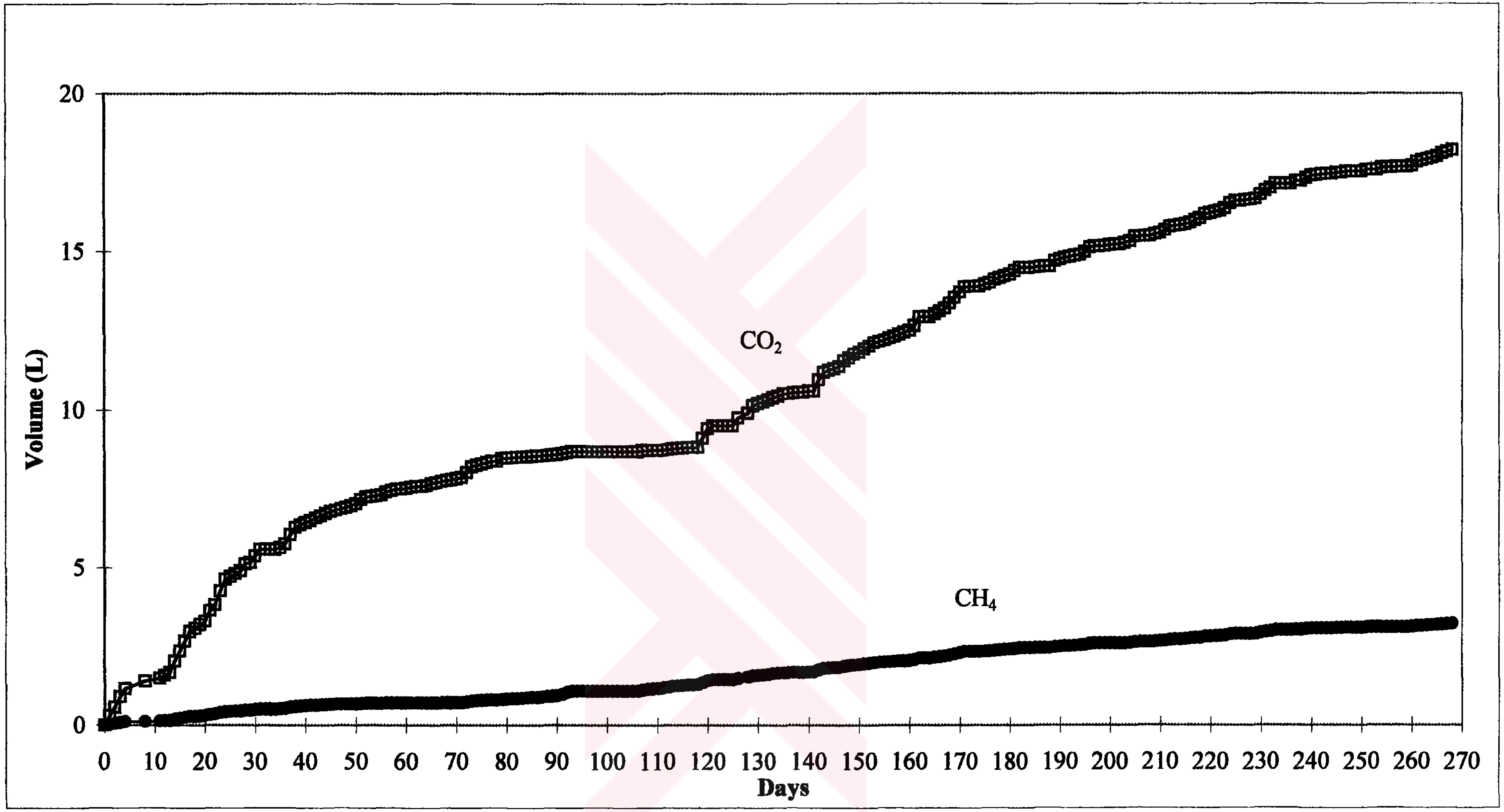


Figure 4.17. Cumulative Methane and Carbon Dioxide Production for the Single Pass Reactor

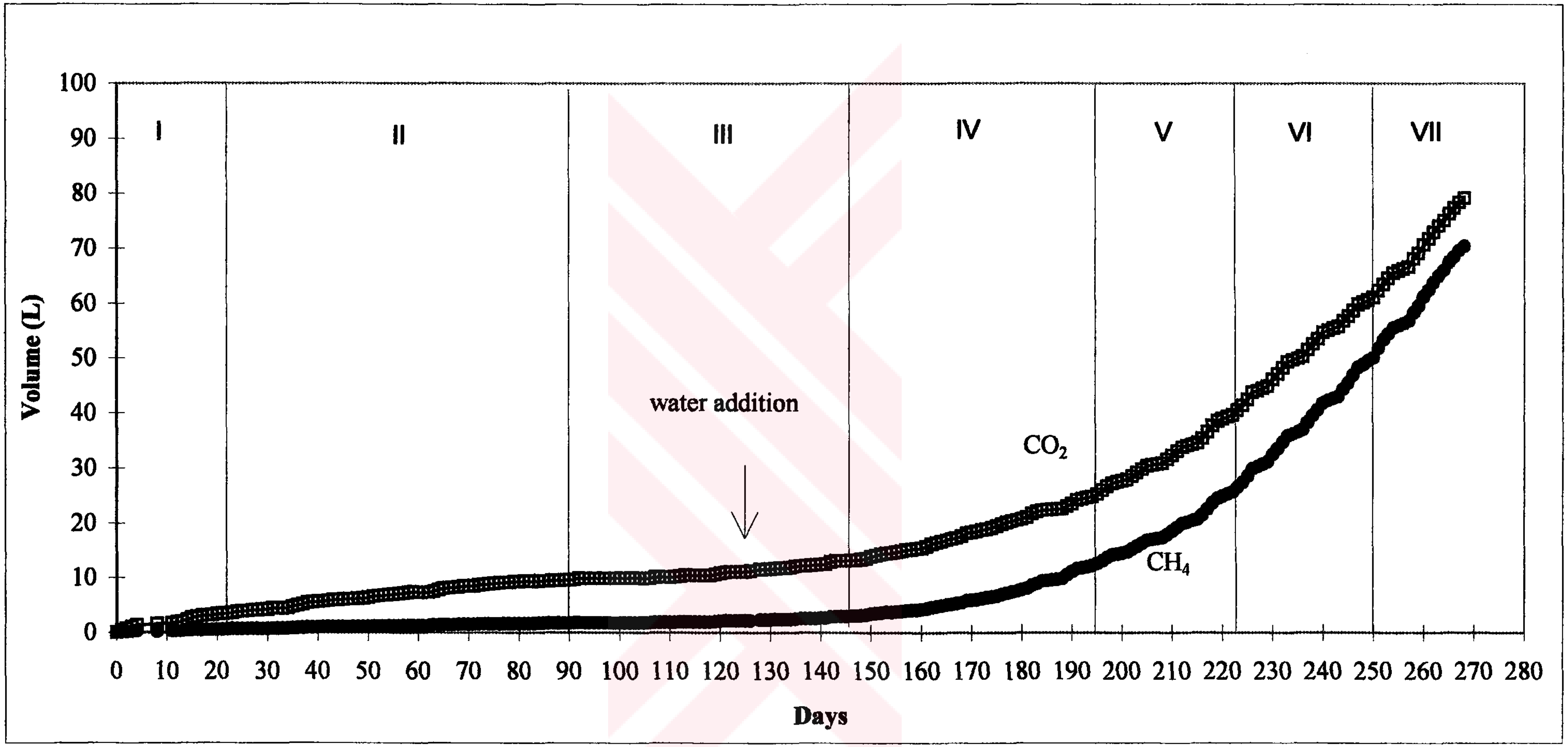


Figure 4.18. Cumulative Methane and Carbon Dioxide Production for the Recycle Reactor

5. SUMMARY AND CONCLUSIONS

The objective of this study was to investigate the effects of leachate recirculation management system on the process of landfill stabilization and leachate treatment. Furthermore, the effect of different moisture application regimes on waste stabilization and leachate treatment was investigated as a another objective of this study. For this purpose, two reactors simulating landfill environment, one with leachate recycle and one as a control reactor, were constructed in the laboratory. Reactors were filled with the shredded synthetic solid waste prepared according to the average municipal solid waste compositions determined for five zones in the city of Istanbul. To investigate the effects of different moisture regimes on waste stabilization and leachate treatment, the recirculation volume and frequency of recirculation were periodically changed throughout the experimental study. In the last phase of the experiment, leachate was buffered prior the recirculation to accelerate the process of waste stabilization. Related to these stated objectives, the results obtained can be summarized as follows:

1. To examine the degree of landfill stabilization and leachate treatment as a consequence of leachate recirculation management strategy employed together with the changes in recirculated leachate volume and recirculation frequency, leachate and gas samples from both columns were analyzed for the following parameters: pH, ORP, COD, ammonia nitrogen, orthophosphate, alkalinity, chloride, sulfate, daily gas production and gas composition.

   a) The pH values obtained from both reactors have shown the similar decreasing trend during the experimental study as a result of volatile fatty acids release after the initial adjustment phase. Slow utilization of the volatile organic acids caused no significant change in the pH in both reactors. Increase in the volume of recirculated leachate did not accelerate utilization of volatile organic acids, therefore having no effect on the pH. Increase in the leachate recirculation frequency showed positive effect in Phase VI, when the slight increase in the pH value from the recycle reactor was observed. The leachate recirculation enhanced the activity of methanogens, resulting in faster volatile organic acids utilization, and thus, pH increase. However, pH of 6.0 was still not favorable for the development of active methanogenic population. An attempt was made to establish environmental conditions favored by methanogens, by buffering the recycled leachate. As a consequence, pH of the system increased to neutral at the end of the experimental study, activity of the methanogenic population was enhanced, and high conversion of volatile acids to methane is observed. Buffering of leachate prior to its recirculation accelerated waste stabilization to a matter of months rather than years.

b) After initial sharp decrease resulted after purging the system with nitrogen gas, ORP values stayed constant at about -50 mV and -70 mV, in the single pass leachate and the recycle leachate, respectively, as a consequence of establishing the actual environmental conditions in the reactor. The increase in the recirculated leachate volume during the Phase III did not effect the ORP values. On the other hand, the ORP values of the recycle reactor began to be more negative throughout the Phases IV, V, and VI as the leachate recirculation frequency increased. The lowest values were monitored during the Phase VI corresponding to the increase in the leachate recirculation frequency from three to four times per week. Buffering leachate prior its recycle resulted in a sharp decrease of ORP identifying the establishment of more reducing environment, favored by methanogenic bacterial population. ORP values of the single pass reactor were remained to be less negative during the experimental period.

c) As a result of solid waste decomposition and the release of organic acids during the Phases I and II, initial COD concentrations were very high. COD concentrations in the leachate from the single pass column happened to reach its peak value faster than the COD concentrations in the leachate from the recycle column as a result of different operating moisture regimes, therefore, indicating the importance of moisture availability for the solid waste decomposition process. The increase in the volume of recirculated leachate throughout the beginning of the Phase III did not seem to effect the COD concentration. However, as a result of water addition in the middle of the Phase III, moisture content increased to the levels ideal for the decomposition of the waste and COD concentration started to decrease. The changes in recirculation frequency throughout the Phases IV to VI enhanced the waste decomposition, reflected by the further decrease in COD concentration and rapid increase in methane concentration. The sharpest decline in the COD concentration and highest methane percentage were obtained during the Phase VI, when leachate recirculation frequency was changed from three to four times per week. Operation procedure employed during the Phase VII, involving a buffering of the recycled leachate prior its recycle, resulted in the establishment of the more favorable environment for the methanogenic population. As a result, utilization of volatile organic acids and decrease of the organic content reached maximum, stabilizing the organic content of the waste matrix. On the other hand, organic strength reduction in leachate from the single pass reactor was not the result of the waste stabilization process. The washout mechanism was responsible for that removal. This was confirmed by observing other indicator parameters of landfill stabilization. While COD concentration showed a decreasing trend, the methane gas concentration remained low, and the ORP and pH values were below then the optimum values for the stabilization of waste.

d) The availability of main nutrients necessary for growth and performance of the microbial population was determined by monitoring ammonia nitrogen and orthophosphate.

The initial increase in ammonia nitrogen concentrations in both reactors during the Phase I was the result of its rapid release caused by the decomposition of the nitrogen containing organic material proceeded. Leachate recirculation reintroduced the ammonia nitrogen leached from the system back, and provided necessary nutrients to the microbial population by enhancing its additional generation. Increased microbial activity in the recycle reactor due to the increase in the leachate recirculation frequency during the Phases IV, V and VI, resulted in the higher utilization of ammonia nitrogen for bacterial assimilation and caused a slight decrease. In contrast to the recycle reactor, the washout mechanism prevailing in the single pass column, caused decrease of ammonia nitrogen concentration. Moreover, ammonia nitrogen concentrations available in single pass reactor throughout the study period was sufficient to maintain nutrient requirements of the system.

Initial decomposition of organic material containing phosphorus resulted in sharp decrease in the leachate orthophosphate concentrations in both reactors. While the increase in recirculated leachate volume did not effect the orthophosphate concentration in the recycle column, the increase in leachate recirculation frequency caused slight decrease in its value. Greater phosphorus utilization in the recycle reactor has proved once more that the leachate recycle directly causes the enhancement of microbial activity. In contrary, decrease in leachate orthophosphate concentration of the single pass reactor confirmed the existence of the washout mechanism.

e) In addition to above mentioned parameters, alkalinity, chloride and sulfate were monitored to better explain the ongoing reactions in the system.

Alkalinity concentrations in both reactors throughout the experimental study was observed to be sufficient to buffer the possible effects of the volatile fatty acids released as a result of decomposition of the waste. While the decrease in the alkalinity concentration in leachate from the single pass reactor was the result of washout in the system, decrease in the alkalinity from the recycle leachate corresponds to decrease in the organic content of the waste, and therefore the decrease of the volatile organic acids.

Monitoring the chloride and sulfate concentrations in the single pass column once more proved the existence of the washout mechanism. Concentration of the chloride, as a conservative trace, was dramatically decreased toward the end of the experiment as a result of washout. At the same time, dispute the unfavorable reduction conditions in the reactor to bring about reduction of sulfate into sulfide, sulfate concentration highly decreased as a result of the washout. On the other hand, dilution effect existing in the recycle column resulted in the slight decrease of the chloride and sulfate concentrations. Highly reducing conditions in Phase VII suggest that conversion of sulfate to sulfide is an additional possible cause of extremely low sulfate concentration at the end of the experimental study.

f) Gas production and its composition monitored during the study period supported the findings from the leachate analysis. Although insufficient isolation of the single pass column reduced the actual daily gas production volume, the results obtained were still comparable. The increase in the recirculated leachate volume did not have any significant effect on the gas production and composition. On the other hand, increase in the recirculation frequency increased gas production and methane concentration. They reaching maximum values during the Phase VI, when leachate recirculation frequency increased from three to four times per week. Buffering of the leachate prior to its recirculation resulted in the highest volumes of gas produced as a consequence of accelerated waste utilization. However, accumulation of the acids and moisture during recirculation days in Phase VII resulted in retardation of methanogenic activity and lower methane and carbon dioxide concentrations. In contrary, washout of the nutrients and organics from the single pass reactor resulted in slow waste utilization, reflected through the low volume of gas produced and low methane concentration.

2. Seeding of the reactors with anaerobic digested sludge at the beginning of the study enhanced the initiation and development of the desirable microbial population in each reactor.

3. The leachate recirculation strategy employed enhanced waste stabilization process in the simulated landfill in terms of the time period required for stabilization and extent of the stabilization. The recycle reactor, whose leachate was contained, buffered and recycled behaved as a controlled anaerobic reactor with promoted contact opportunity for bacteria with substrate, nutrients and moisture. On the other hand, leachate from the single pass reactor was constantly removed, taking away necessary nutrients and substrate from the system. As a result, environment in the recycle reactor was more uniform and more suitable for biomass development then that in the single pass reactor.

4. Increase in the recirculated leachate volume from 1L to 2L did not show any effect on the extent of waste stabilization and leachate treatment. Since it was believed that further increase in the recirculated leachate volume would cause unnecessary flooding

in the system, increase in recirculation frequency was studied until the end of the experimental period.

5. The frequency of leachate recirculation has proved to be an important factor for high degree of organic release and their removal. Recirculation frequency was gradually increased during the study, to obtain the optimum number of recirculations necessary to provide the highest waste stabilization and leachate treatment. Taking into the consideration the cost of pumping in full scale applications of leachate recirculation, four times per week recirculation was estimated to be the maximum appropriate recirculation frequency. Although every attempt to increase frequency of recirculation was followed by the positive changes in the monitored parameters, the best results were obtained with four times per week recirculation practice.

6. When four times per week recirculation is practiced in longer run, some operational problems, such as clogging and/or flooding, may occur. As observed in this study, such problems will result in accumulation of volatile acids, and will lower the efficiency of the process, lowering pH and methane concentrations.

7. Leachate buffering prior recirculation established environmental conditions favored by methanogenic population responsible for conversion of organics to methane and carbon dioxide. Combination of leachate buffering with four times per week recirculation provided high degree of waste stabilization and leachate treatment as reflected by gas volume produced, and leachate indicator parameters. In cases when four times per week recirculation practice cause clogging or flooding problems, buffering the leachate prior to its recirculation play important role in maintaining neutral pH values in the system.

8. One of the objectives of this study was to determine the effects of leachate recirculation on waste stabilization and leachate treatment. Knowing that the waste stabilization is directly related to the amount of methane produced, determination of methane generated per kilogram of organic matter stabilized is taken as an indicator of stabilization degree.

In order to estimate the degree of stabilization for single pass and reactor column theoretical and actual methane yield were calculated and compared. Furthermore, the percentage of COD converted to methane in the process of waste stabilization was determined. For theoretical methane yield determination, the biodegradability approach was preferred over stoichiometric approach because of two reasons; firstly, individual organic constituents found in solid waste were not known, and secondly, the biodegradability approach takes the extent of biodegradability into consideration, making obtained results more reliable.

In order to determine methane yield for single pass and recycle reactors, procedure used by Güleç [35] was followed.

The biodegradability of the solid waste in the single pass and recycle column was determined from the mass of COD removed during the experimental study. The maximum and minimum COD concentrations, as well as the moisture available in the reactors at the beginning and the end of the study period in the single pass and recycle column are presented in the Table 5.1.

Table 5.1. Data used for the determination of COD mass removal

	COD_{MAX} (mg/L)	INITIALLY AVAILABLE MOISTURE (L)	COD_{MIN} (mg/L)	FINALLY AVAILABLE MOISTURE (L)
Single Pass	44,337	7.0	11,333	7.3
Recycle	46,325	6.75	9,538	5.8

COD mass removal is calculated as follows:

<u>Single pass:</u>

$$\text{COD mass removal} = \left(\frac{(44{,}337\text{mg}/\text{L}*7\text{L}) - (11{,}333\text{mg}/\text{L}*7.3)}{44{,}337\text{mg}/\text{L}*7\text{L}} \right) \times 100 = 73\%$$

Recycle:

$$\text{COD mass removal} = \left(\frac{(46{,}325\text{mg}/\text{L}*6.75\text{L}) - (9538\text{mg}/\text{L}*5.8)}{44{,}337\text{mg}/\text{L}*6.75\text{L}} \right) \times 100 = 82\%$$

The values used for the estimation of theoretical methane yield are given in the Table 5.2.

Table 5.2. The values used for the Estimation of Theoretical Methane Yield

REACTOR	MOISTURE CONTENT (%)	COD MASS REMOVAL (%)	gr COD/ gr organic matter	METHANE YIELD /gram COD (L/gr)
Single Pass	78	73	1.2	0.35
Recycle	75	82	1.2	0.35

Using these data;

Single Pass:

1 ton of municipal solid waste =

$$10^6\text{gr} \times (1-0.78)\frac{\text{gr dry weight}}{\text{gr wet weight}} \times 0.73\frac{\text{gr organic weight}}{\text{gr dry weight}} \times 1.2\frac{\text{gr COD}}{\text{gr organic matter}}$$
$$= 0.1927 \times 10^6\text{grCOD}$$

If 1 gr COD = 0.35 L CH_4 at $0^{O}C$ and 1 bar, than;

Methane Yield = 0.1927 x 10^6 gr COD x 0.35 L CH_4 / gr COD = 67 L CH_4/kg solid waste

Recycle:

Using the same procedure, methane yield is calculated to be 86 L CH_4/kg solid waste.

On the other hand, actual volume of methane generated throughout the experimental study is determined to be 0.24 L/kg solid waste and 6 L/kg solid waste for the single pass and recycle reactor, respectively. These findings are presented in

Table 5.3.

Table 5.3. Theoretical and Actual Methane Yields for the Single Pass and Recycle Reactor

REACTOR	THEORETICAL METHANE YIELD		ACTUAL METHANE YIELD	
	(L CH_4/kg SW)	L CH_4	(L CH_4/kg SW)	L CH_4
Single Pass	67	871	0.24	3.12
Recycle	86	1118	6	78

The volume of methane produced can be converted to COD using the following expression [15];

$$COD_{CH4} = V_{CH4} \times 2.875 \text{ g COD/L } CH_4$$

Using actual methane yield values;

Single Pass:

$COD_{CH4} = 3.2 \text{ L} \times 2.875 \text{ g COD/L } CH_4 = 11.37 \text{ gr}$

Recycle:

$COD_{CH4} = 78 \text{ L} \times 2.875 \text{ g COD/L } CH_4 = 224.25 \text{ gr}$

Using the values from the Table 5.1, maximum mass of COD released is determined to be 323.66 gr and 312.69 gr for single pass and recycle reactor, respectively. From these and the values calculated above it can be easily seen than 3.5 percent of COD in leachate from the single pass reactor is converted to methane, while the same value for recycle reactor is 71 percent.

When theoretical and actual methane yield are compared, it can be seen that the actual methane yield is much lower then it was expected to be. Actual methane yield was determined to be only 0.35 percent and 6 percent of the theoretical values for the single pass and recycle reactor, respectively. Such a great difference between actual and theoretical values was due to the two main reasons; insufficient capacity of gas collection units, and insufficient isolation of single pass reactor causing one-way gas diffusion from the system. As a result, actual daily gas productions for single pass and recycle reactor were determined to be lower than it should be, therefore directly effecting the calculations of actual methane yield.

Although values given here can not be compared on the quantitative level, they can be used for the qualitative analysis. From the theoretical methane yield computations, it can be seen that recycle column had a greater potential for the methane production. This is in some way supported by the actual values obtained. Leachate recirculation provided environment suitable for faster degradation of organic matter and higher production of methane. Of 73 percent COD removed in single pass column only 3.5 percent was converted to methane, while of 82 percent COD removed in recycle column 71 percent was converted to methane. These numbers strongly support the fact that washout is prevailing mechanism existing in single pass column, and not the actual stabilization process. On the other hand, 71 percent conversion to methane is a proof that waste stabilization process is accelerated as a result of leachate recirculation technique employed.

Based upon experimental results obtained during the investigation, the following conclusions are provided:

1. The reactor system designed and operated to simulate landfill environment, as an controlled anaerobic bioreactor with leachate recirculation, provided accelerated stabilization of waste matrix and *in situ* leachate treatment.

2. The degree of waste stabilization and efficiency of COD removal was dependent on the operational stages. While changes in volume of recirculated leachate did not have any effect on the system, change in the recirculation frequency positively

effected the stabilization process and leachate treatment efficiency. Leachate recirculation increased moisture content in the system creating better contact opportunities between substrate and microorganisms. As a result, increase in leachate recirculation frequency accelerated stabilization process within the recycle column.

3. Leachate recirculation management strategy employed four times per week, may cause operational problems in the long run. Operational problems, such as clogging and flooding lower the process efficiency by lowering pH and methane concentrations.

4. Leachate recirculation with pH control further enhanced landfill stabilization and treatment efficiency, reducing time required for stabilization to a matter of months rather than years. In case when increased recirculation frequency cause operational problems in the long run, buffering the leachate prior to its recirculation is important to maintain the desired pH values in the system.

5. The leachate recirculation management strategy employed enhanced waste stabilization occurring in the simulated landfill in terms of the extent of stabilization obtained, as a reflection in higher volume of gas produced, gas composition (i.e. increased methane gas concentrations) and other leachate indicator parameters.

6. Leachate recycle improved the homogeneity of the biochemical environment needed for anaerobic waste degradation that may effectively shorten the time normally required for waste stabilization.

7. Recycling of leachate promoted development of internal mechanisms responsible for waste stabilization and leachate treatment. Reintroduction of necessary nutrients such as phosphorus and nitrogen, enhanced the growth of microbial population and effected the extent of stabilization.

8. Leachate recycle provides a moist environment, rich with nutrients that positively effect gas production rates. Volumes of gas produced were significantly increased when leachate recycle was employed, having higher percentages of methane concentrations.

This research showed that landfill leachate management with leachate recirculation is a promising and challenging strategy. Leachate recirculation is a feasible way to treat the leachate *in situ*, and, therefore, decrease the cost of further external treatment. This research showed that four times per week recirculation strategy provide highest degree of waste stabilization. However, it is noted that practicing the four times per week recirculation in full scale, may cause some operational problems, such as flooding or clogging, specially in areas with increased precipitation. This observation is confirmed on the full scale, in study performed in Seamer Carr Landfill Site in UK [29]. Increased volumes of leachate recirculated caused increase in water levels inside the landfill and leachate seepage over the edge of the liner. Furthermore, increased volumes of leachate resulted in formation of hard-pan of solids on the waste surface reducing the infiltration and forming the surface ponding.

Combination of different operational regimes may be the best to achieve the optimum waste stabilization. Four times per week recirculation frequency may be employed right after the landfilling of solid waste to raise its moisture content to field capacity, establish viable microbial population and therefore shorten the time necessary to initiate decomposition process. However, landfill operator should be aware of possibility of organic overload and accumulation of volatile organic acids, that may inhibit the development of viable methanogenic population. Therefore, to avoid possible adverse effects, leachate pH adjustment prior to its recirculation is recommended. After significant methane concentrations are obtained, as a result of initiated decomposition process, recirculation frequency may be lowered to one or two times per week. Furthermore, taking into consideration the season and the climate, recirculation frequency may be changed, so that four times per week recirculation using spraying system would be appropriate in summer months when maximum leachate loss due to the evaporation may be achieved. On the other hand, in fall and winter months, one or two times per week recirculation would be appropriate to prevent possible flooding, surface ponding, or freezing conditions.

6. RECOMMENDATION

Leachate recirculation management strategy may be employed in modern landfills in Turkey by making necessary modifications in existing landfills, and taking necessary safety precautions. The data obtained from this study are results of bench scale laboratory work with constant operational conditions. A full scale study is recommended to confirm the results obtained.

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APPENDIX A

A - Sample calculations for determination of the moisture losses during gas production [15]

The calculation of the moisture losses during gas production are based on the following assumptions: (1) the total system pressure is equal to 1 atmosphere, (2) the volume of gas collected is saturated with moisture, and (3) the density of water is 1000 g/L.

The volume of moisture lost due to the gas production can be calculated using the following expression:

$$V_{LOST} = \frac{q * \rho_{GAS}}{MW_{H_2O} * 55.6 Moles / L} \qquad (1)$$

where;

V_{LOST} = Volume of liquid lost due to gas production [L H_2O/ L gas],

q = Specific humidity [g H_2O/ g gas],

ρ_{GAS} = Gas density [g/L],

MW_{H20} = Molecular weight of water [18.015 g/mole].

The specific humidity, which is mass of water vapor contained within the unit mass of moist space, can be calculated using the following expression:

$$q = \frac{0.622 * (VP)}{P_T - [0.378 * (VP)]} \qquad (2)$$

where;

VP = Water vapor pressure at specified temperature (kN/m^2),

P_T = Total system pressure (101.325 kN/m^2)

At 34°C water vapor pressure is estimated to be 5.495 kN/m^2. When substituted in equation (1) specific humidity is calculated to be 0.0344 g H_2O/g gas.

The gas density may be calculated using the ideal gas law, provided that molecular weight of gas in known. Molecular weight of gas is calculated from the following equation:

$$MW_{GAS} = MW_{CH4}*X_{CH4} + MW_{CO2}*X_{CO2} \qquad (3)$$

where;

MW_{GAS} = Molecular weight of gas mixture [g/mole],

MW_{CH4} = Molecular weight of methane [16.043 g/mole],

MW_{CO2} = Molecular weight of carbon dioxide [44.010 g/mole],

X_i = Mole fraction of gas_i [moles gas/total moles of gas]

Using Henry's law mole fraction of carbon dioxide and methane at 34 °C are calculated to be 1.151 x 10^{-4} and 1.25 x 10^{-6}, respectively. Substituting the values in the equation (3) molecular weight of gas is calculated to be 2.64 x 10^{-4}. Therefore, gas density is calculated to be:

$$\rho_{GAS} = \frac{MW_{GAS}*P_T}{R*T} = \frac{2.64\times10^{-4}*1}{0.0821*(273+34)} = 0.0344\ gH_2O/g\ gas \qquad (4)$$

where;

R = Universal gas constant [0.0821 L*atm/K*mole],

T = Temperature [K].

By substituting the findings from the equations (4) and (2) into the equation (1), volume of liquid lost due to the gas production is calculate to be 9.09 x 10^{-9} L H_2O/ L gas. Knowing that single pass column produced 68.97 L of gas, volume of liquid lost due to gas production in single pass column is determined to be 6.27 x 10^{-7} L.

The same procedure is used for determination of volume of liquid lost due to gas production from the recycle column.