SUSTAINABLE SOLID WASTE MANAGEMENT AND IN-SITU ATTENUATION MECHANISMS IN LANDFILLS UNDER AEROBIC AND ANAEROBIC CONDITIONS

by

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Dedicated to my father, Şenol Erses and my mother, Birsen Erses

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ABSTRACT

Up to date, several laboratory and pilot-scale investigations of different landfill concepts have been carried out to achieve sustainability by reducing long term landfill emissions. Leachate recirculation, flushing bioreactor, pre-treatment and aeration methods are evolved to obtain a low-emission landfilling alternative. Through the continued developments of these methods, the aerobic landfill concept which depends on aerobic degradation of municipal solid waste is a new perspective on waste landfilling and suitable way to minimize environmental impacts.

Therefore, the objective of this study was to obtain information about aerobic and combination of aerobic and anaerobic digestion of solid waste in landfills in order to evaluate and determine an efficient and cost-effective landfill management system. The proposed research was focus mainly on to find optimal conditions for solid waste degradation and better understand the attenuation mechanisms for carbon, nitrogen, sulfur and heavy metal by using aerobic, anaerobic, aerobic pretreated and aerobic remediated landfill concepts. With this goal, four landfill bioreactors were operated under aerobic and anaerobic conditions in a thermo-insulated room at a constant temperature of 32 ºC. Reactors were filled with the shredded synthetic solid waste of 19.5 kg prepared according to the average municipal solid waste compositions determined in İstanbul and operated under wet-tomb management strategy by using leachate recirculation. Aerobic conditions in the reactor were developed by using an air compressor.

The results of this study showed that aeration in municipal solid waste landfills is a viable management option for the accelerated stabilization of a waste matrix. Aeration is a feasible way to treat the leachate *in situ*, and, therefore, decrease the cost of further external treatment. Aeration of the waste mass provides rapid removal of organics, nitrogen and phosphorus. Aerobic pretreated and aerobic remediated bioreactor landfill concepts were also more efficient in terms of waste stabilization and leachate treatment when compared to the anaerobic bioreactor.

ÖZET

Günümüze kadar, düzenli depolama sahalarının uzun süreli çevresel etkilerini azaltmak ve sürdürebilirliğini başarmak için farklı işletme koşullarına sahip düzenli depolama sahası konseptleri labarotuvar ortamında ve pilot ölçekli sahalarda araştırılmıştır. Düşük kirletici yüküne sahip düzenli depolama sahası elde etmek için sızıntı suyu geri devri, aşırı su ile yıkama, ön arıtma ve aerobik ayrışma metotları geliştirilmiştir. Bu metotların gelişmesi devam ederken, katı atığın hava verilerek ayrışması prensibine dayalı havalı (aerobik) düzenli depolama konsepti, düzenli depolama alanında yeni bir bakış açısı ve çevresel etkileri minimize eden uygun uzaklaştırma yöntemi olarak ön plana çıkmıştır.

Bu çalışma havalı (aerobik) ve havasız (anaerobik) prosesleri kullanarak en verimli ve ekonomik katı atık düzenli depolama yönetim sistemini geliştirmeyi amaçlamaktadır. Araştırma, öncelikle katı atığın ayrışması için optimum şartları bulmaya odaklanıp, karbon, azot, sülfür ve ağır metallerin farklı işletme koşullarında giderme mekanizmalarını gözlemlemeyi hedeflemektedir. Bu amaç kapsamında düzenli depolama sahalarını simüle eden 4 adet reaktör havalı, havasız, havalıdan havasıza ve havasızdan havalıya çevrilmek üzere laboratuvar ortamında 32ºC sabit sıcaklık altında işletilmiştir. Reaktörler, İstanbul Bölgesi için belirlenen ortalama katı atık kompozisyonuna göre sentetik olarak hazırlanmış 19.5 kg katı atık ile doldurulmuş ve sızıntı suyu geri devredilerek işletilmiştir. Havalı şartlar ise reaktöre kompresörden basılan hava ile sağlanmıştır.

Bu çalışmanın sonucunda, havalandırmanın düzenli depolama sahalarında katı atık stabilizasyonunu hızlandırdığı gözlenmiştir. Ayrıca, havalandırma sızıntı suyu içerisindeki kirleticileri saha içerisinde arıttığından, ek sızıntı suyu arıtma ihtiyacını ve masrafını azaltmıştır. Havalı reaktörde organik maddenin, azotun ve fosforun hızla giderildiği gözlenmiştir. Sızıntı suyu geri devirli havalı-havasız ve havasız-havalı reaktörler, havasız reaktörle karşılaştırıldığında atık stabilizasyonu için gerekli zamanı kısaltması, sızıntı suyu kirletici yükünü azaltması bakımından daha etkin verime sahiptir.

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		Units
COD	Chemical oxygen demand	mg/L
BOD	Biochemical oxygen demand	mg/L
TOC	Total organic carbon	mg/L
TS	Total solid	mg/L
TVS	Total volatile solid	mg/L
VFA	Volatile fatty acids	mg/L

1. INTRODUCTION

Municipal solid waste (MSW) landfills are generally operated by conventional landfilling techniques, where anaerobic conditions are created within the landfill waste. However, decomposition of solid waste may cause environmental problems if emission of landfill gas is not controlled and landfill leachate seeps down to the groundwater. Under anaerobic conditions within a landfill site, the stabilization process is slow and may increase the potential risks to human health and the environment (Hudgins and March, 1998). According to Kruempelbeck and Ehrig (1999), the long term environmental impact caused by municipal solid waste (MSW) landfills may last for centuries. As a result, more stringent regulations for monitoring landfills, in addition to their design and operation, are needed. Recent European regulations on waste management are primarily intended to reduce the use of landfilling, mainly because of problems generated by the above mentioned environmental impacts. In order to achieve these goals, the Landfill Directive adopted by the European Union (EU) requires that the amount of biodegradable MSW going to the landfill should be reduced by 25 percent until 2002, 50 per cent by 2005 and 75 per cent by 2010 (Council of the European Union, 1999). In spite of extensive laws and regulations to reduce the waste quantity and emissions, landfilling is still the most commonly employed disposal method worldwide since it is a comparatively simple and economic way for solid waste disposal. Moreover, landfilling is the ultimate disposal method for wastes that can not be recovered.

Conventional sanitary landfills consist of cells and lifts with liners, drains, gas vents, leak detection systems with intermediate and final covers. On the other hand, due to inadequacies of conventional waste management practices, extensive lab-scale and full-scale investigations have been carried out to answer the essential questions of low-emission landfilling. Increasing attention is being given to the enhancement of waste stabilization by leachate recirculation to reduce the time required for waste degradation, improve leachate quality and enhance the rate of gas production. Bioreactor landfill systems as a modification of conventional landfill with the addition of leachate recirculation were developed to minimize environmental impacts through optimizing waste degradation. Here, leachate is collected, stored and reinjected back into the landfill to promote in situ anaerobic biological degradation. The advantages of leachate recirculation have been demonstrated by many researchers that performed numerous lysimeters and field tests (Pohland, 1980; Titlebaum, 1982; Kinman et al., 1987; Doedens and Cord, 1989; Otieno, 1994; Townsend et al., 1996; Chugh et al., 1998; El-Fadel, 1999; Pohland and Kim, 1999 and 2000; Onay and Pohland, 1998; San and Onay, 2001; Erses and Onay, 2003). In addition to leachate recycling, the positive effects of sludge, nutrient and buffer additions on solid waste degradation have been demonstrated by many researchers (Buivid et al., 1981; Craft and Blakey, 1988; Leuschner, 1989; Kayhanian et al., 1996, Çınar, 2001).

Over the last few years a new perspective on landfilling solid waste has .. which involves aerobic landfill technology to rapidly stabilize and detoxify the waste, reduce methane gas, volatile organic compounds and odor emissions as well as eliminate off site leachate treatment needs (Purcell, 2000a and 2000b; Read et al., 2001a and 2001b; Jacobs et al., 2003; Kim, 2005; Cossu et al., 2003). In spite of the recent practices on aerobic landfilling, the effect of in situ aeration has not been well defined from the view point of the attenuation mechanism of contaminants during the stabilization period. Until today all field research has taken place using existing landfill sites, so that many of the sites that are run as full-scale aerobic landfills have used waste that has been anaerobic for some time. There are questions yet to be answered about the behaviour of waste that has never been anaerobic (Read et al., 2001a; Rich et al., 2007). This study aims to better understand and evaluate stabilization mechanisms occurring at landfill sites. In sustainable landfill management systems, economy is also vital as efficiency. In the case of aerobic landfill, initial capital and operation costs are higher. This situation forced the researchers to develop new landfill concepts by using limited aeration.

Therefore, the objective of this study was to investigate about aerobic and combination of aerobic and anaerobic digestion of solid waste in landfills in order to evaluate and determine an efficient and cost-effective landfill management system. The proposed research focuses mainly on finding optimal conditions for solid waste degradation and better understand the attenuation mechanisms for carbon, nitrogen, sulfur and heavy metal by using aerobic, anaerobic, aerobic pretreated and aerobic remediated landfill concepts.

1. LITERATURE REVIEW

The literature review has been divided into two main sections: (1) municipal solid waste management with a special emphasis on landfilling (2) landfill stabilization and factors affecting landfill stabilization.

2.1. Municipal Solid Waste Management

The amount and types of municipal solid wastes have increased gradually because of economical and technological developments. Sustainable management of increasing amounts of these solid wastes has become a major social and environmental concern. The practice of the three R's (reduction, reuse, recycle) fits very well within the sustainable development concept. The waste hierarchy has taken many forms over the past decade, but the basic concept has remained the cornerstone of most waste minimisation strategies (Figure 2.1). The aim of the waste hierarchy is to extract the maximum practical benefits from products and to generate the minimum amount of waste (www. defra.gov.uk /environment/waste/).

Figure 2.1 Waste management hierarchy (www. defra.gov.uk /environment/waste/)

Improper solid waste management leads to substantial negative environmental impacts (pollution of air, soil and water) and health and safety problems (diseases spread by insects and rodents attracted by garbage heaps and diseases associated with different forms of pollution). Integrated solid waste management (ISWM) is a concept that goes beyond the safe disposal of wastes and suggests optimization of the waste hierarchy. It addresses the solution of wastes problem by emphasizing the notion of “Cradle to Grave” responsibility (Williams, 1998). The system boundary model for the integrated solid waste management (ISWM) is shown in Figure 2.2. The model evaluates the environmental burdens associated with waste management from the point at which a material is discarded into the waste stream to the point at which it is either converted into a useful material or, it is finally disposed. Nonetheless, often there are many difficult situations that face municipal managers in planning and directing concrete ISWM projects in cost-effective, technically sound and politically favorable manners (White, Franke and Hindle, 1995).

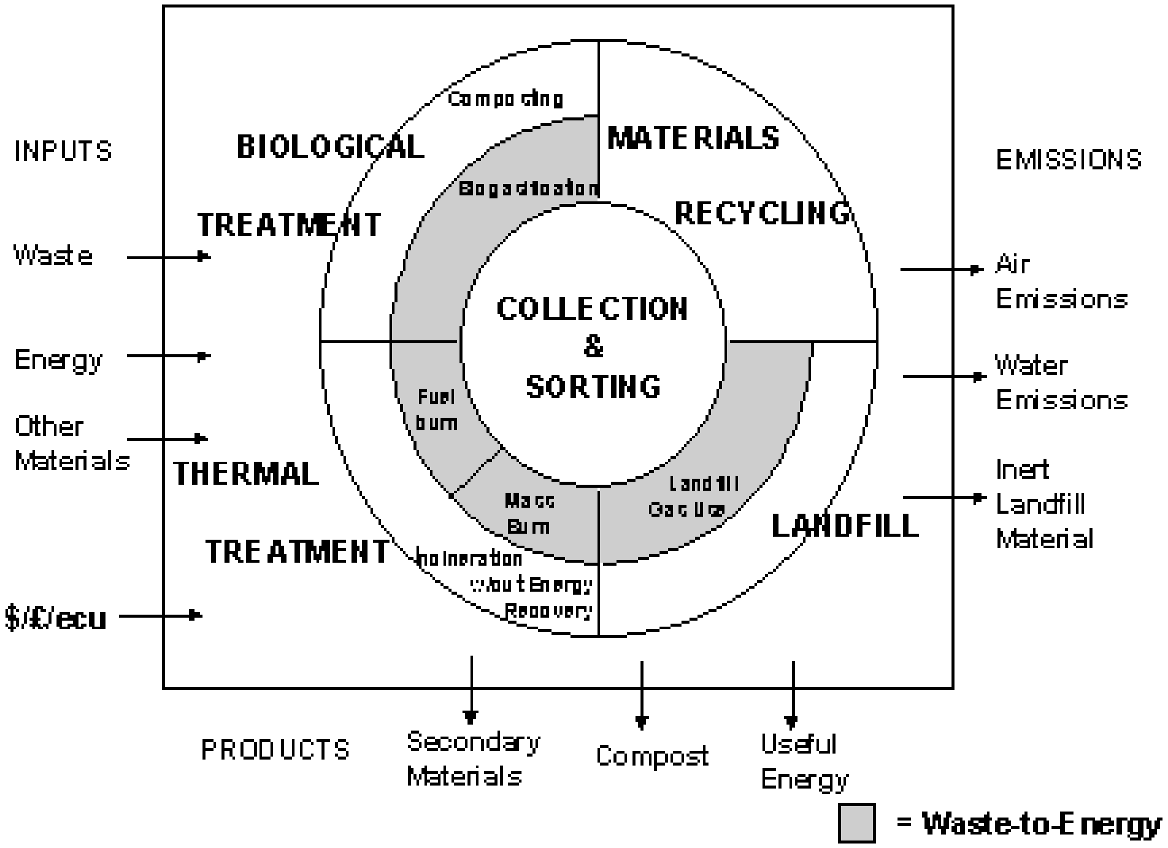


Figure 2.2. The element of integrated waste management (White, Franke and Hindle, 1995).

The composition of solid waste is a crucial element for defining waste management strategies. Moreover, knowledge on the composition of waste is essential for implementing the most appropriate waste reduction policies and for choosing the adequate waste treatment and disposal processes. In Table 2.1. different MSW compositions in different countries are given (Girgin, 2004).

Table 2.1. Municipal solid waste composition in different countries (all data are % in weight)

Material Groups	England	Germany	Greece	Syria	China	USA	Japan
Organic Matter	19.8	44	48.5	72.5	60.0	27.5	32.0
Paper	34.8	17.9	22.0	5.0	3.1	41.1	38.0
Plastic	11.3	5.4	10.5	5.1	4.5	7.5	11.0
Glass	9.1	9.2	3.5	0.6	0.8	8.0	7.0
Metal	7.3	3.2	4.2	0.8	0.3	9.4	6.0
Others	12.2	20.3	11.3	16.0	31.3	6.5	7.0

The majority of the municipal solid waste in Turkey is organic (Table 2.2). Organic components can be assumed to be 50-55%, whereas recyclable and others (ash and slag, dust etc.) can be assumed to be 20-25% (Metin, Erozturk and Neyim 2003).

Table 2.2. Municipal solid waste composition in major cities of Turkey (%, in weight)

	Istanbul	Bursa	İzmir	Mersin	Adana
Organic	43.0	53.1	46.0	63.0	64.4
Recyclable	33.9	36.4	31.0	29.4	25.2
Paper/board	7.8	18.4	12.0	18.42	14.8
Plastics	14.2	11.6	12.0	6.69	5.92
Metal	5.8	3.0	3.0	1.25	1.4
Glass	6.2	3.4	4.0	3.08	3.08
Others	23.1	10.5	23.0	7.6	11.4

The global practices of ISWM vary from region to region, country to country, and from one municipality to another, depending upon the prevailing specific conditions (natural, social, economic etc.) (Girgin, 2004). Table 2.3 provides an overview of some wastes management practices in several industrialized countries. As can be seen from Table 2.3, there are many methods such as incineration, waste minimization, waste recovery and recycling to reduce the volume of the solid wastes however landfilling has been the most widely adapted practice for municipal solid waste management worldwide, because landfilling has been considered to be the simplest and most economically attractive of all available solid waste management options.

Table 2.3. Solid waste management practices in some countries

Countries	**kg generation /capita-day**	**Landfilling %**	**Incineration %**	**Composting %**	**Recycling %**
Canada	1.65	80	6	4	10
Germany	0.95	45	35	4	16
Italy	1.1	75	13	7	5
Japan	1.26	15	60	5	20
Spain	0.95	65	5	17	13
Switzerland	1.2	10	58	10	22
UK	1.15	85	8	2	5
USA	1.98	65	10	2	23

In Turkey, 81 provinces have a total of 3215 municipalities, 16 of which metropolitan municipalities. Generally, 33% of wastes are disposed in 13 sanitary landfills, 1% is being composted in 3 composting plants and the rest is being disposed using non-conventional methods like dumping, burning etc. While the average solid waste generation was 0.6-0.7 kg/capita-day in 1990, today this amount is calculated as 1.32 kg/capita-day in summer, 1.34 kg/capita-day in winter and 1.33 kg/capita-day for yearly average. It is estimated that the annual amount of solid wastes collected in the whole country is almost 26.12 million tones per year (SIS, 2003). Figure 2.3 represents disposal methods applied the collected waste in the country. As seen in Figure 2.3, only a small fraction of the generated waste is composted or incinerated, and the unprocessed part is sent directly to waste disposal sites. While the numbers of sanitary landfills are increasing, especially with the new sites operating in certain large cities, the amount of sanitary landfilling is still less than 50%. Disposal of municipal solid waste into uncontrolled garbage dumps that are not properly regulated is the most important problem regarding solid waste management in Turkey. On the other hand, inappropriate removal methods such as open burning or pouring into rivers of MSW that can pose risk to both environmental impact and public health are still being applied. Percentages of employed disposal methods in different countries are represented in Table 2.3. When disposal strategy in Turkey is compared to other countries, it is revealed that the application of appropriate methods like landfilling, incineration or composting is crucially insufficient in Turkey.

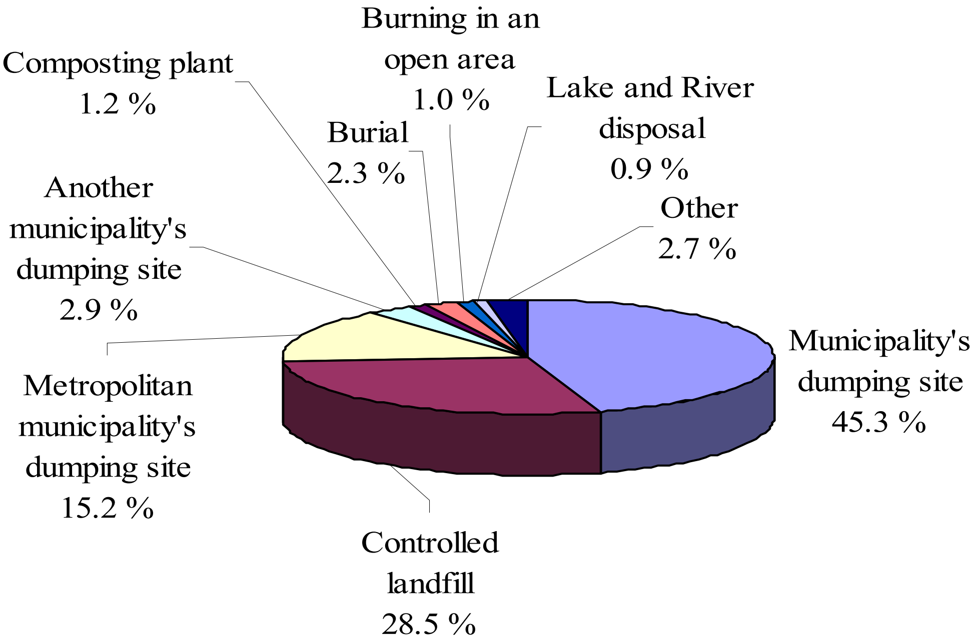


Figure 2.3. Municipal solid waste disposal in Turkey (SIS, 2003).

On the other hand, increasing population growth and societal demands for more conveniences and a higher standard of living have increased solid waste management challenges, often resulting in a critical need for expanded landfill capacity. Moreover, the generation and unwanted migration of landfill gas and leachate due to the waste degradation processes cause significant environmental pollution. As a result of this, there is increasing demand for more stringent regulations for monitoring landfills in addition to their design and operation. The most recent European regulations on waste management are primarily intended to reduce the use of landfilling, to control landfill emissions and their effects (including green house effect) and to shorten the long term environmental impact (aftercare phase). In order to achieve these goals, the Landfill Directive adopted by the EU Council of Ministers on 26 April 1999 requires that the amount of biodegradable MSW going to landfill should be reduced, with 25 per cent diverted from landfill by 2002, 50 per cent by 2005 and 75 per cent by 2010 (Council of the European Union, 1999). In spite of extensive laws and regulations to reduce the waste quantity, considerable amounts of solid waste have to be expected in future and landfilling will be the most commonly employed disposal method worldwide since it is a comparatively simple and economic way for solid waste disposal. Moreover, landfilling is the ultimate disposal method for wastes that can not be recovered. In Turkey, municipal waste is controlled by regulation on Control of Solid Wastes with the aim of assessing any adverse impacts. Landfilling is the the major process used for the treatment of municipal solid waste. The responsible authorities for solid waste management in Turkey are the ministry of Environment and Forestry and municipalities.

2.1.1 Sanitary Landfilling

A landfill, also known as a dump, is a site for the disposal of waste materials by burial and is the oldest form of waste treatment. Until the 1900s, solid waste was directly dumped on the land. In the 1920s and 1930s, sanitary landfills refers to those where municipal solid waste is disposed of, were first constructed to replace the open dumps that posed, and some continue to pose, significant threats to human and environmental health. These primitive landfills were, literally, naturally occurring depressions in the landscape that were filled with waste and then covered with a minimum amount of soil. Sand and gravel pits and borrow areas were also commonly filled to form primitive landfills. Therefore, in the past, the term sanitary landfill was used to denote a landfill in which the waste placed in the landfill was covered at the end of each day’s operation. Today, sanitary landfill refers to an engineered facility for the disposal of MSW designed and operated to minimize public health and environmental impacts (Tchobanoglous et al., 1993; Makinabakan,1999). Sanitary landfills can be conceptualized as biochemical reactors in which physical, chemical and biological processes are taking place and the processes result in the generation of landfill gas and leachate.

2.1.1.1. Gas Production and Quality. Landfill gases including mainly CO_2 (carbondioxide) and CH_4 (methane) result from the anaerobic decomposition of the solid waste. In addition, traces of other gases (N_2, O_2, CO, H_2S) and volatile organic compounds (VOCs) are found in landfills and their productions and qualities depend on the microbiological system, moisture content, refuse age and composition.

Methane usually accounts for 40-60 % of the total gas production in a landfill (Pohland et al., 1987). The gas is colorless, odorless, soluble in water and lighter than air (Tchobanoglous et al.,1993). Methane can be explosive when it is present in the air in concentrations between 5 and 15 percent and implicated as a greenhouse-effect gas. Carbon dioxide is also soluble in water and can produce carbonic acids, lower pH, and cause mineralization in groundwater. Hydrogen sulfides production often causes odor problem and can also react with heavy metals. In conclusion, it forms precipitates and clogs underdrain systems (Al-Yousfi and Pohland, 1998). Volatile organic compounds can be toxic although present small quantities.

In addition to potential environment risk related to the production and migration of gases from waste during landfilling, knowledge of landfill gas production and quality indicates degree of landfill stabilization. To predict the total gas production, theoretical models, plus data from lysimeters and full scale landfills have been developed including stoichiometric methods and weighted biodegradability methods (Ham and Barlaz, 1989; Pohland et al., 1987).

The stoichiometric methods based on a representative chemical formulation for municipal solid wastes. The total volume of gas can be estimated using the representative chemical formula given in Equation 2.1 (Tchobanoglous et al., 1993).

$$C_aH_bO_cN_d + \left(\frac{4a-b-2c+3d}{4}\right) H_2O \rightarrow \left(\frac{4a+b-2c-3d}{8}\right) CH_4 + \left(\frac{4a-b+2c+3d}{8}\right) CO_2 + dNH_3 \tag{2.1}$$

The weighed biodegradability methods based on assumption of biodegradability. An example of this approach is given (Güleç, 1999). An average municipal solid waste contains 35% of moisture content and 75% of degradable organic matter on dry basis and it has a specific COD value of 1.2 gr COD per gr dry organic matter. When these figures are taken into consideration, the yield is expressed as below;

$$1 \text{ ton MSW} = 10^{6} \text{ g} * (1-0.35)\frac{\text{g dry weight}}{\text{g wet weight}} * 0.75 \frac{\text{g organic weight}}{\text{g dry weight}} * 1.2 \frac{\text{g COD}}{\text{g organic matter}}$$

$$= 0.585 \times 10^{6} \text{ g COD}$$

An assumption is made at this point from a theoretical relation between COD and methane;

$1 \text{ g COD}_{\text{organic matter}} = 0.35 \text{ L CH}_4$ at 0°C and 1 bar (Speece, 1995)
By using this assumption;

$$Y_{\text{methane/kg solid waste}} = 0.585 \times 10^{6} \text{ g COD} \times 0.35 \text{ L CH}_4/\text{g COD}_{\text{organic matter}} = 205 \text{ L/kg MSW}$$

From the therotical methods, the total and methane gas production range between 120-460 L/kg dry waste and 60-250 L/kg dry waste, respectively whereas, actual total and methane gas production from lysimeters and full scale landfills range between 1-250 L/kg and 1-70 L/kg, respectively.

2.1.1.2. Leachate Generation and Characteristics. Leachate is a liquid that has percolated through the refuse mass and has extracted dissolved and suspended components (Rachdawong,1994). Leachate generation is a function of the external sources such as rainfall, ground water, surface runoff and the decomposition of solid waste in landfills.

The formation of leachate depends on 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 (Korfiatis et al., 1984). After field capacity is reached, leachate will be generated. The amount of leachate may be predicted by water balance methods or computer simulation models such as the Hydrologic Evaluation of Landfill Performance

(HELP) (Quasim and Chiang, 1994). The water balance method involves summing the amount of water entering the landfill and subtracting the amounts of water lost from landfill to predict leachate

$$\text{Leachate}=P-SR-SMS-AET \tag{2.2}$$

Where,
P=precipitation; SR=surface runoff; SMS= change in soil moisture storage; AET= actual evapotranspiration

Although the quantity of leachate is an important consideration, the quality of leachate is also important since it depicts stabilization process and affects the selection of the treatment system. The quantity and quality of leachate produced depend on the factors including solid waste composition, age of the refuse, operation of the landfill, climate, hydrogeologic conditions in the vicinity of landfill site, conditions within the landfill such as chemical and biological activities, moisture content, temperature, pH and degree of stabilization (McBean, Rovers and Farquhar, 1995).

Leachate characteristics change as MSW stabilization in landfill proceed. Leachate can be characterized as a young and old depending upon the phase of landfill stabilization. Acid phase of landfill stabilization is characterized with young leachate, exhibiting low pH, high organic content as indicated by BOD_5, COD, TOC, total volatile acids (TVA) and an abundance of mobilized ions. Old leachate mainly indicates the methane fermentation phase and the leachate exhibits reduced TVA, high pH values, reduced readily degradable organic components and the presence of humic and fulvic-like compounds. Characteristics of leachate from old and young landfill are given in Table 2.4.

Table 2.4. Leachate characteristics (Tchobanoglous et al., 1993).

Constituents (mg/L)	Young Landfill (less than 2 years)		Old Landfill (greater than 10 years)
	Range	Typical	
BOD_5	2,000-30,000	10,000	100-200
TOC	1,500-20,000	6,000	80-160
COD	3,000-60,000	18,000	100-500
Total Suspended Solid	200-2,000	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 $CaCO_3$	1,000-10,000	3,000	200-1,000
pH	4.5-7.5	6	6.6-7.5
Total Hardness as $CaCO_3$	300-10,000	3,500	200-500
Calcium	200-3,000	1,000	100-400
Magnesium	50-1,500	250	50-200
Potassium	200-1,000	300	50-400
Sodium	200-2,500	500	100-200
Chloride	200-3,000	500	100-400
Sulfate	50-1,000	300	20-50
Total iron	50-1,200	60	20-200

2.1.1.3 Leachate Management Strategies. Two principal leachate management strategies exist for landfill operations; They are single pass leaching with leachate containment, collection and *ex-situ* treatment, and leachate containment, collection and recirculation back into the landfill for *in-situ* treatment.

Ex-situ leachate management strategy. *Ex-situ* or single pass leachate management entails containment, collection and removal of leachate from the site for *ex-situ* treatment. As a result of leachate quantity and quality, there are a number of options for treatment of leachate; on-site full treatment, on-site pretreatment and disposal to a publicly owned treatment work (POTW), and transport off-site to a POTW directly (McBean, Rovers and Farquhar,1995).

Because the characteristics of the collected leachate vary so widely during landfilling, it is very difficult to recommend a specific treatment process. Therefore, a leachate treatment system constructed to treat a young leachate has different set of treatment processes than one constructed to treat an old leachate (McBean, Rovers and Farquhar, 1995). That was confirmed by Chian (1977) who investigated the stability of organic matter using membrane ultrafiltration, gelpermeation chromatography and specific organic analyses in landfill leachates. The results showed that the majority of the organics consisted of free volatile fatty acids. The next largest group is a fulvic-like material with a relatively high carboxyl and aromatic hydroxyl group density and finaly, a small percentage of organics consisted of high molecular weight humic-carbohydate-like complex. In conclusion, free volatile fatty acid fraction decreased, fulvic and humic-like materials increased with increasing age of landfill and it was recommended that leachate from a recently generating landfill is best treated by microbial processes such as anaerobic and aerobic, whereas, organic in stabilized leachate are preferably removed by physical-chemical processes.

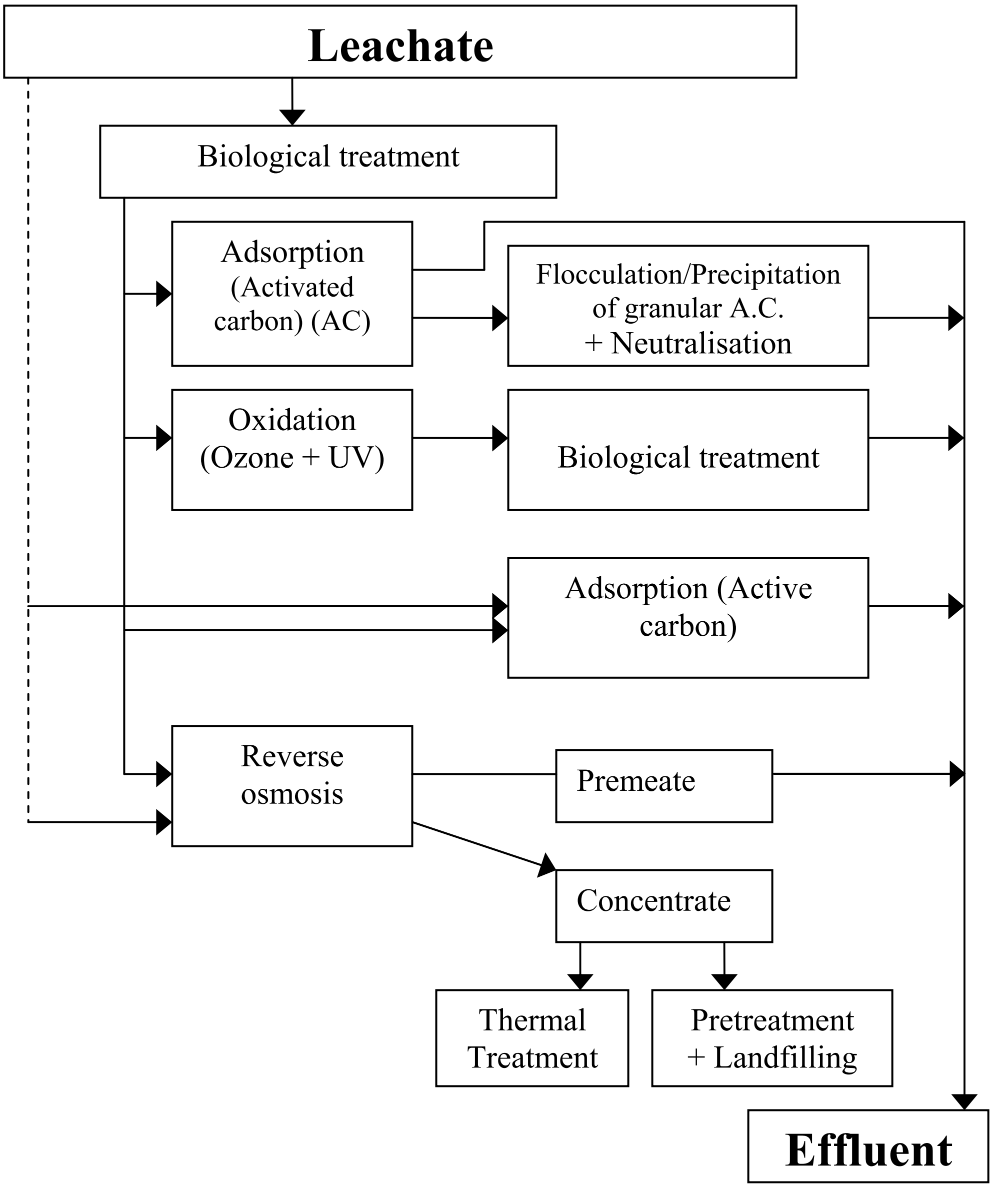
Physical-chemical treatment methods such as activated carbon adsorption, chemical precipitation, ion exchange and reverse osmosis may become an attractive option for landfill leachate treatment, either as a preliminary to biological treatment or as a complete treatment especially for leachate from an older landfill. Keenan, Steiner and Fungaroli (1983) conducted a full-scale physical-chemical treatment of raw sanitary landfill leachate in southeastern Pennsyvania. The treatment sequence consists of equalization, lime precipitation, sedimentation and air stripping of ammonia. It was concluded that the complete physical-chemical treatment sequence achieved the following removals: 48-69% of the organic matter, ammonia-N and total kjeldahl-N; 70% of the suspended solids, and 50% or beter of the heavy metals except copper, for which removal efficiency was 37.9%.

As concluded by Iza, Keenan and Switzenbaum (1992), a young landfill leachate is amenable to anaerobic treatment for its organic fraction, but special care should be taken with the management of the inorganic compounds, especially heavy metals since high heavy metal concentration in leachate inhibit the anaerobic process. Therefore, physical-chemical treatment is generally required prior to the biological processes to remove the metals.

Because of variations in leachate quantity and characteristic, the external treatment of leachate requires a combination of biological, chemical and physical treatment methods instead of one method. Typical combinations are shown in Figure 2.4. Therefore, treatment costs increase a function of leachate strength, quantity and available disposal options.

Furthermore, with the continous hardening of discharge standards in most countries and the ageing of landfill sites with more and more stabilized leachates, conventional treatments (biological or physico-chemical) are not sufficient anymore to reach the level of purification needed to fully reduce the negative impact of landfill leachates on the environment. Therefore, in the last 20 years, more effective treatments based on membrane technology has emerged as a viable treatment alternative to comply and pending water quality regulations in most countries (Renou et al., 2008).

Pirbazari et al. (1996) used a hybrid technology known as the ultrafiltration-biologically active carbon (UF-BAC) process that amalgamates adsorption, biodegradation and membrane filtration. The process efficiencies were in the range of 95-98% in terms of TOC reduction, and exceeded 97% for specific organic pollutants. Contrary to conventional systems, nitrifiers or organisms which are able to degrade slowly biodegradable substances are not washed out of the system and no loss of process activity occurs.



------ : potential treatment for leachate from the methanogenic phase of a landfill

AC: Activated Carbon

UV: Ultraviolet Light

Figure 2.4. Schemes of often used methods and combinations for leachate treatment (Stegmann et al., 2005)

Reverse osmosis (RO) seems to be one of the most promising and efficient methods among the new processes for landfill leachate treatment. RO performances on separation of pollutants from landfill leachate were reported higher than 98% removal for COD and 99% for heavy metal concentrations (Linde and Jonsson,1995; Bilstad and Madland, 1992). However, two issues have been identified, and remain today, as major drawbacks for the implementation of pressure-driven membrane processes, and particularly RO, to landfill leachate treatment: membrane fouling (which requires extensive pretreatment or chemical cleaning of the membranes, results in a short lifetime of the membranes and decreases process productivity) and the generation of large volume of concentrate (which is unusable and has to be discharged or further treated) (Renou et al., 2008).

In-situ leachate management strategy. Leachate recirculation management entails the containment, collection and reinjection of leachate back into the landfill to promote in-situ anaerobic biological treatment. Increasing attention is being given to leachate recirculation because it enhances the decomposition of organic matters in landfills. Therefore, leachate recirculation may be used (Warzinski et al., 2000)

- To maximize waste disposal capacity
- To incease waste degradation and gas production and improve waste stabilization
- To increase leachate management and treatment flexibility
- To improve leachate quality
- To reduce leachate treatment cost

These advantages of leachate recirculation have been demonstrated by many researchers that performed numerous lysimeters and field tests (Pohland, 1975; Pohland,1980; Titlebaum, 1982; Kinman et al., 1987; Otieno,1994; Townsend et al., 1996). The treatment of leachate by continuous recirculation provides very promising results in term of organic matter but it cannot answer to complete treatment of other waste constituents. Therefore, Diamadopoulos (1994) investigated the physico-chemical treatment of recirculation stabilized sanitary leachate and it was observed that coagulation-precipitation studies yielded maximum COD removal 56% for iron, 39% for aluminum and 18% for lime at optimum pH 4. Powdered activated carbon adsorption at pH 4 results in final COD concentrations around 300 mg/L while air stripping of ammonia was very efficient, removing 95% of ammonia.

Leachate recirculation increases the moisture level of the solid waste and provides accelerated landfill stabilization. Microbial activity is increased at higher moisture content (Bae et al., 1998). Churg et al. (1998) investigated the effect of recirculated leachate volume on waste degradation. Volume of recirculated leachate was selected to be 2, 10 and 30 percent of the initial volume of waste bed in the reactors and the exchange of leachate between an existing batch of stabilized waste and a batch of fresh waste was applied until establishing a balanced microbial population in the fresh waste. Therefore, the experiments show that the rate and extent of waste decomposition improved with the increase in moisture flow. Another similar study was conducted by San (1999) in two simulated landfill reactors, one single pass and one recycle, to understand the effect of recirculation, recirculated leachate volume and recirculation frequency on stabilization processes. The experimental results indicated that recirculation provided accelerated stabilization of waste matrix and *in situ* leachate treatment. Changes in volume of recirculated leachate did not have any effect on the system, whereas, change in the recirculation frequency positively effected the stabilization process and leachate treatment efficiency.

Leachate recirculation accelerates the conversion and transformation of both organic and inorganic constituents. Pohland et al. (1993) reported that leachate recirculation provides attenuation of heavy metals with rapid waste stabilization. Onay and Pohland (1998) reported that utilization of leachate recirculation enhanced stabilization in the reactors by increasing the uniformity of moisture, substrate and nutrient distrubition and 95 percent of nitrogen conversion is achieved by in situ nitrification and denitrification.

Field studies in the literature confirmed lysimeter studies and demonstrated the successful application of leachate recycle as an in situ treatment option. Doedens and Cord (1989) investigated the influence of recirculation using different recirculation methods and design concepts in 13 large-scale landfills in Germany. The methods include spray tankers and horizontal distribution pipes. The results showed faster reduction of BOD and COD in landfills commencing leachate recirculation few years after beginning of landfilling operations.

Another full scale study was done in Nework, Ohio by Owens-Corning Fiberglas Corporation that produces a variety of glass fiber insulation products for the housing, automotive, appliance and industrial building markets. The results indicated that leachate recycling shortened the stabilization time of industrial solid waste (Merritt, 1992).

In addition, one study is conducted by Townsend et al. (1996) in North-Central Florida. Leachate was recirculated to the landfill using infiltration pond leachate recycle system. Samples of leachate, gas and landfilled solid waste during a four-year period indicated that the leachate recycle system increased moisture content of the solid waste and enhanced the degradation by promoting suitable conditions for biological stabilization.

Although positive effects have been reported on solid waste degradation, high recirculation rates may adversely affect anaerobic degradation of solid wastes. For instance, Ledakowicz and Kaczorek (2004) observed that leachate recirculation can lead to the inhibition of methanogenesis as it may cause high concentrations of organic acids ($pH<5$) which are toxic for the methanogens. Furthermore, if the volume of leachate recirculated is very high, problems such as saturation, ponding and acidic conditions may occur (Chan et al., 2002).

2.1.2. Sanitary Landfill Management Systems

The modern sanitary landfill is truly an important component of today's integrated solid waste management system. Two management systems, conventional waste management and bioreactor landfill operation, may be employed in sanitary landfills to eliminate the potential environmental risk of leachate and gas production.

2.1.2.1 Conventional Landfill Management. Sanitary landfills worldwide are experiencing the consequences of conventional landfilling techniques, whereby anaerobic conditions created within the landfill promotes slow stabilization of the waste, methane gas production (an explosive, "green house" gas) and generation of leachate (which can pollute groundwater) over long periods of time (Hudgins 2000). A conceptual layout of a conventional landfill is presented in Figure 2.5. (http://www.schulich.ucalgary.ca /Civil/csce_calgary/2006/Landfill-biorectorLandfills.pdf). To decrease the environmental risks, the cells and lifts of conventional landfills are designed with liners, drains, gas vents, leak detection systems, intermediate and final covers and also wastes are kept dry in landfills to minimize production of leachate and landfill gas. However, a 30-year post-closure period is the minimum necessary to effectively manage the long-term environmental liabilities of the organic components, salts and heavy metals contained within conventional "dry" landfills. According to some researchers, the long term environmental impact caused by municipal solid waste (MSW) landfills may last for centuries because a significant portion of the biodegradable fraction of waste placed in conventional MSW landfills remains relatively unstabilized following decades of landfilling (Rathje, 1999; Kruempelbeck and Ehrig, 1999). The containment provided by these landfills offers environmental protection initially; however, at some point beyond the 30-year period, there may be partial failures of the containment lining system, leading moisture infiltration which increases in leachate and gas production.

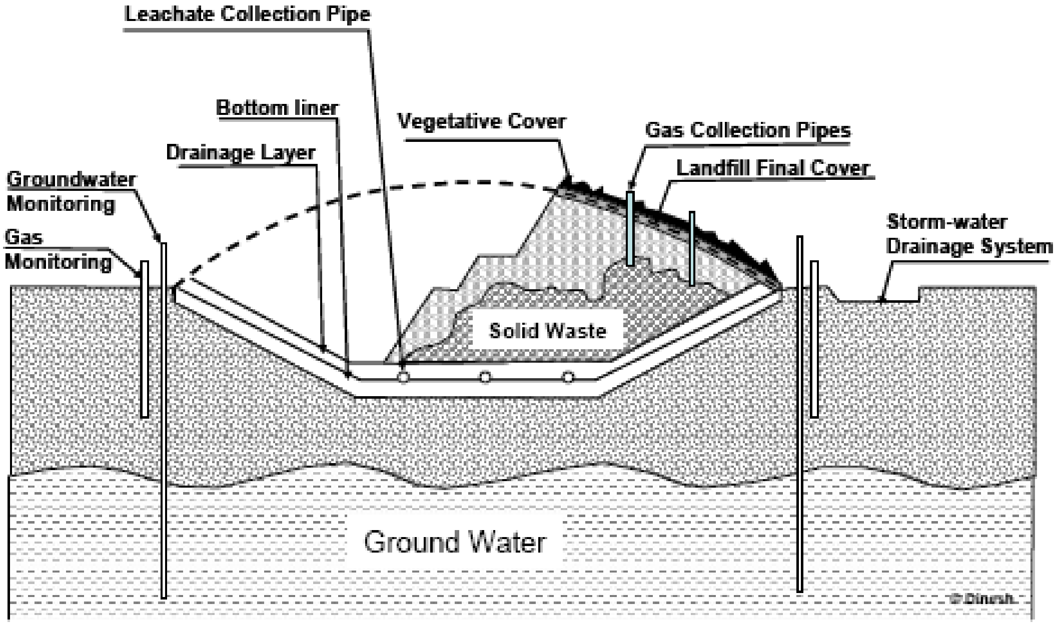


Figure 2.5. General layout of conventional landfill (http://www.schulich.ucalgary.ca)

Conventional landfilling includes monitoring of the incoming waste stream, placement and compaction of the waste, and installation of landfill environmental monitoring and control facilities. However, the inadequacy of conventional waste management, have led the development of bioreactor landfills which provide rapid, complete attenuation of solid waste constituents and enhance gas recovery.

2.1.2.2. Bioreactor Landfill Management. A bioreactor landfill is a sanitary landfill that uses enhanced microbiological processes to transform and stabilize the decomposable organic waste within 5 to 10 years of implementation, compared to 30 to 100 years for "dry" conventional landfills. A bioreactor landfill is operated as controlled anaerobic or aerobic digester. Waste materials enter the process, than additional materials are added to accelerate decomposition (Walsh and O'Leary 2002). Sludge, nutrient, buffer and liquid are added to enhance and benefit from the sequential phases of waste stabilization. The addition of moisture (leachate, water) is common to bioreactors in order to optimize and accelerate the microbially mediated waste transformation reactions throughout the landfill complex (Pohland 1980). Moisture addition is generally supplied by leachate recirculation. The numerous advantages of leachate recirculation include uniform distribution of nutrients and microorganisms, pH buffering, dilution of inhibitory compounds, liquid storage, and evaporation opportunites at low additional construction and operating cost (Reinhart and Townsend 1998).

While a variety of operational approaches have been tested to accelerate waste degradation, bioreactors can be categorized into three types or groups: anaerobic bioreactors, aerobic bioreactors, and hybrid bioreactors. Bioreactor landfills have traditionally been operated as anaerobic systems, where the existing microorganisms responsible for waste degradation and landfill gas (CH_4 and CO_2) are encouraged to thrive. Another approach that has more recently been suggested is the addition of air to landfills so that the landfill becomes an aerobic bioreactor (Stessel and Murphy 1992). In both anaerobic and aerobic conditions, leachate is recirculated into waste matrix.

Potential advantages of bioreactors include:

- Decomposition and biological stabilization of MSW in shorter period of time
- Lower waste toxicity and mobility due to both aerobic and anaerobic conditions
- Reduced leachate disposal costs
- A 15 to 30 percent gain in landfill space due to an increase in density of waste mass

- Significantly increased landfill gas generation that, when captured, can be used for energy
- Reduced post-closure care

Anaerobic bioreactor. Anaerobic bioreactor landfill is the modification of conventional landfill with the addition of leachate recirculation and gas management systems (Pohland, 1990). Figure 2.6 indicates the design and operational features of anaerobic bioreactors. Degradation of solid waste in landfills is rate-limited by insufficient moisture. The average landfilled municipal solid waste has a moisture content of only 25% wet weight (Emcon Associates, 1980). However, Farquhar and Rovers (1973) found that the maximum methane production in landfills occurred at moisture content of 60-80% wet weight. This suggests that most landfills are well below the optimum moisture content for methane production. Moisture content can be most practically controlled via leachate recirculation. Leachate recirculation management entails the containment, collection and reinjection of leachate back into the landfill to promote *in situ* anaerobic biological treatment. The advantages of leachate recirculation have been demontrated by many researchers that performed numerous lysimeters and field tests (Pohland 1980; Titlebaum; 1982; Kinman et al., 1987; Doedens and Cord-Landwehr 1989; Otieno 1994; Townsend et al., 1996; Churg et al., 1998; El-Fadel 1999; Pohland and Kim 1999 and 2000; Onay and Pohland 1998; San and Onay 2001; Erses and Onay 2003; Agdag and Sponza, 2004). Moreover, waste stabilization in landfill may be accelerated by using one of the following techniques; pH control by buffer addition, nutrient addition, sludge addition, shredding and temperature management. However, successful implementation requires the development of these techniques. The single most important and cost-effective method is liquid addition and management.

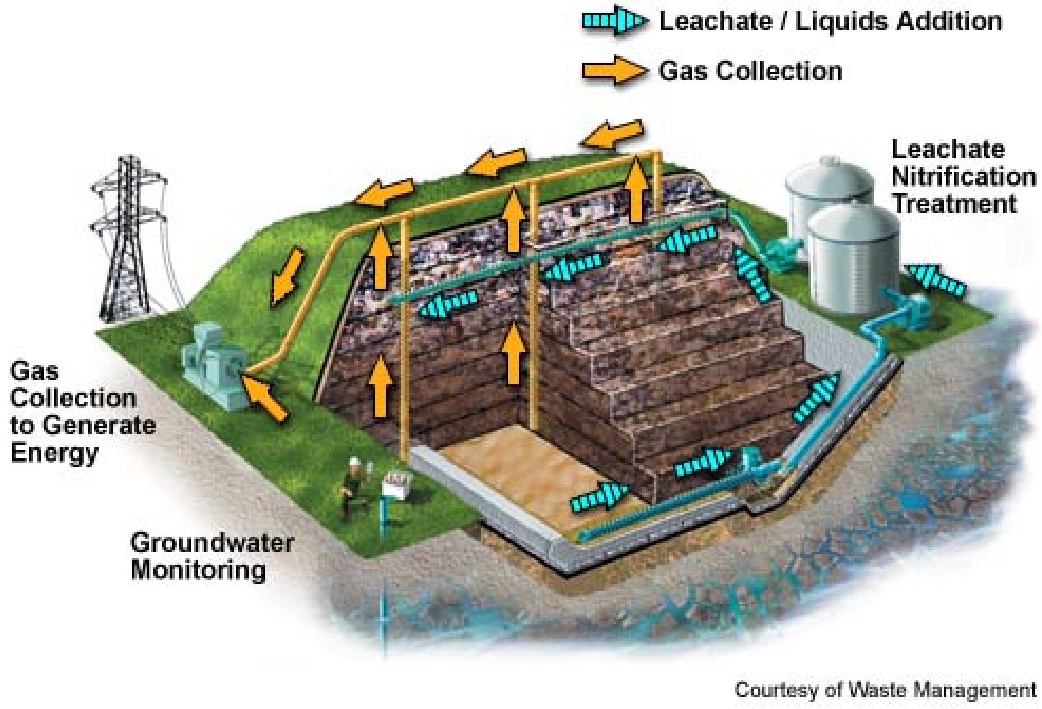


Figure 2.6. The design and operational features of anaerobic bioreactors. (http://www.wm.com/wm/environmental/bioreactor/bioreactorbrochure.pdf)

San and Onay (2001) conducted a research to understand the effect of recirculation processes by using two simulated landfill reactors, one conventional landfill and one bioreactor landfill. The experimental results indicated that recirculation provided accelerated stabilization of waste matrix and *in situ* leachate treatment. On the other hand, El-Fadel (1999) conducted field scale experiments to evaluate biodegradation and refuse settlement rates with the effect of leachate recirculation in the Mountain View Landfill in California. As a result of monitored parameters including total volumetric gas production, gas composition, internal refuse temperature, cell settlement and leachate level within the cell, it was demonstrated that leachate recirculation enhanced gas generation and methane yield and increased settlement rates.

It seems more practical to modify an existing landfill operation to accelerate decomposition while maintaining the critical, physical elements of the landfill. Therefore, the current approach to bioreactors is to devise a system in which water is introduced into the waste to wet the material as uniformly as possible. The added moisture then accelerates decomposition of MSW, which generates large landfill gas quantities. According to Pacey 1989, leachate recirculation enhances methane gas generation. Chugh et al. (1998) reported that with increased moisture content rate of methane production increase by 25 to 50 percent. In their experiment the obtained methane yield was 0.13 m^3/kg VS added. Townsend et al. (1996) 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 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 (Reinhart and Townsend, 1998).

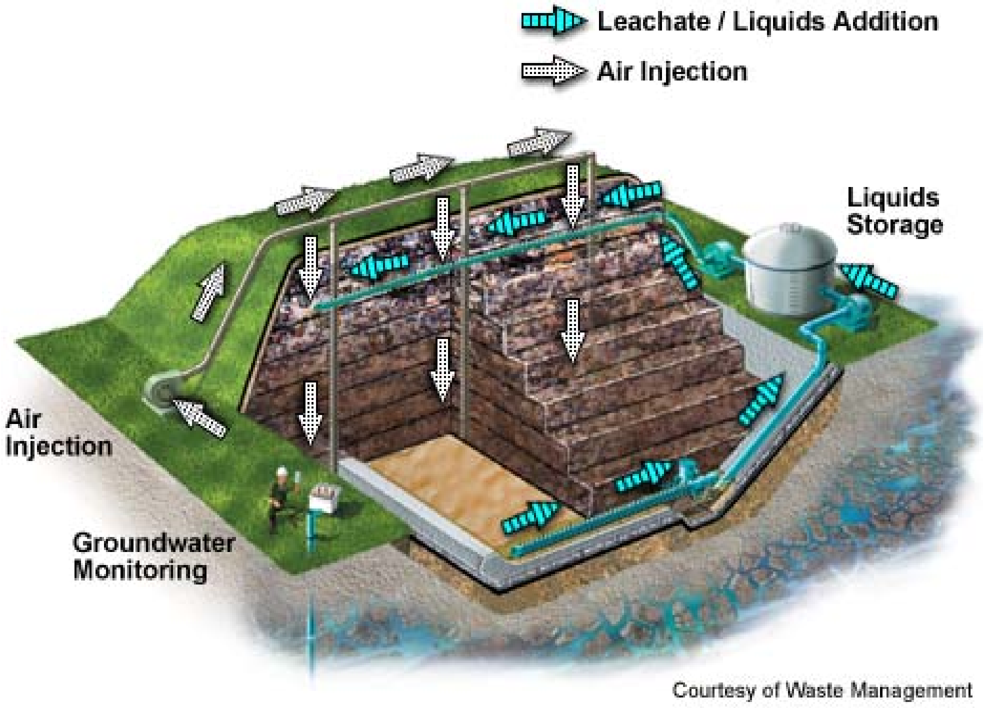
Benefits of anaerobic bioreactor landfills include;

- Leachate storage within the waste mass,
- Increased rate of landfill settlement
- More rapid waste stabilization than conventional landfills
- Increased methane generation rates
- Potential for limited landfill mining
- Lower postclosure costs

There are several methods of reintroducing leachate into the landfill environment depending on specific site conditions; spray irrigation, surface application, vertical well injection and horizontal well injection are some of them. Factors such as ease and cost of installation, waste quantity, and climate affect the method selection.

The intensive monitoring of anaerobic bioreactor landfills is essential. The amount of gas generated, methane concentration, pH of leachate reaching the landfill base and the other measures (such as volatile organic acids, alkalinity) that describe the biochemical reactions taking place within the landfill can be used to analyze operating conditions. For example, if the waste is wetted too rapidly, a buildup of volatile organic acids might lower the leachate pH, inhibiting the methane-producing bacteria and reducing the rate of biodegradation.

Aerobic bioreactor. Active aerobic biodegradation process, such as composting, has demonstrated for years that the biodegradable portion of solid waste can be stabilized in a significantly shorter time by providing the proper proportions of air and moisture (Purcell 2000b). This lead to evaluation of *in situ* aerobic biodegradation of municipal solid waste in a landfill environment to achieve optimum waste stabilization in terms of stabilized organic matter, decreased concentrations of leachate contaminants, eliminated methane generation and waste mass subsidence. Aerobic bioreactors are operated by controlled injection of moisture and air into the waste mass through a network or horizontal and/or vertical wells (Figure 2.7).



Courtesy of Waste Management

Figure 2.7. The design and operational features of aerobic bioreactors. (http://www.wm.com/wm/environmental/bioreactor/bioreactorbrochure.pdf)

The effectiveness of aerobic bioreactor depends on waste mass temperature and moisture that are maintained within optimal ranges (Hudgins and Read 2001). This is accomplished by balancing airflow and leachate recirculation rate into the waste mass in a manner that effectively stabilizes the waste in a much shorter time frame than under anaerobic conditions. Improper balancing of air and leachate can lead to poor aerobic landfill performance and, possibly, elevated waste mass temperatures. For that purpose, Stessel and Murphy (1992) made a lysimeter study to determine the quantities of moisture and air that would optimize waste degradation. Seven galvanized steel and four PVC lysimeters were runned at different air flow and leachate recirculation rates and it was found that waste moisture levels should be maintained at 75 % for optimum degradation. The required application rate of leachate as a flux was 0.09 m^3/m^2-day and aeration requirement was 40.000 m^3 of air per cubic meter of water applied. The results also indicated that leachate COD (Chemical Oxygen Demand) concentrations were reduced by 90 % in the aerobic cell compared to the anaerobic control cell and volatile solids were reduced by 60 % in 40 days. In other related work, Leikam et al. (1997) indicated that methane concentration in landfill gas could be reduced from 60% to 10-15 % in 7-10 days by air injection, indicating the potential for final site stabilization.

Aerobic techniques have been used successfully in many countries worldwide, with a range of aims. In the United States aerobic landfill techniques can be used to save a large void space for ongoing use as landfill. It has been proposed that aeration be combined with landfill mining, which would lead to landfills with longer lifespans; many researchers regard this as a type of sustainable landfill (Read et al., 2001 a). In Germany, aerobic landfilling is used to bring forward stabilization (Stegmann et al., 2003). Accelerated stabilization can reduce leachate and gas emissions to below the levels required for completion. In Italy, pre-treatment, aeration and flushing is combined to optimize the advantages of each of the three technologies (Cossu et al., 2003). In the Netherlands aeration has been used to achieve odour reduction prior to re-opening an old landfill (Jacobs et al., 2003).

Ritzkowski and Stegmann (2003). Emission Behaviour of Aerated Landfills: Hazen and coworkers (2000) investigated the critical physical, chemical and biological processes that control aerobic landfill bioremediation under the leachate recirculation. Experiments were carried out in the laboratory by using 55-gallon plexiglass lysimeters containing paper (40% by weight), food waste (12%), garden waste (10%), glass (9%), plastic (8%), metal (7%), wood (3%) and others (11%). Lysimeters were constructed as wet aerobic, wet anaerobic, dry anaerobic and dry anaerobic converted to wet aerobic. According to the primary results, aerobic, wet tanks indicate more subsidence, increased biodegradation rate, decreased level of leachate contaminant than the anerobic tanks.

Cossu et al. (2003) conducted a lab-scale research to investigate different landfill concepts for achieving sustainability by reducing long-term landfill emissions. Laboratory tests were carried out using six plexiglass columns which simulate traditional anaerobic landfill, mechanical-biological pretreatment, landfill aeration with forced and natural advective air flow (semi-aerobic), flushing and the combination of mechanical-biological pretreatment, aeration by the semi-aerobic method, and Flushing (PAF model). A comparison of the emissions from the six lab columns indicate that the traditional anaerobic landfill with MSW has the highest level of emissions (high BOD,COD and ammonia) and delayed biodegradation. Stabilization is accelerated by mechanical-biological treatment and the total gas production is much higher than unprocessed waste. Flushing of waste rapidly reduces the level of emissions for all parameters tested. Aeration of waste, either with forced or natural advective air flow, produces a rapid and marked oxidation of organics and nitrogen. The combination of pretreatment, semi-aerobic conditions and flushing (PAF model) achieves a more marked and quicker reduction of the concentration of COD, TKN and ammonia in leachate.

Kim (2005) compared aerobic and anaerobic landfills with respect to gas and leachate quality, fate or metals, settlement behavior and biodegradation of lignocellulosic materials. Four stainless- steel lysimeters were used as simulated landfills. Through air injection, a large enhancement of waste decomposition was observed. More than 90% of the maximum chemical oxygen demand (COD), biochemical oxygen demand (BOD) and total organic carbon (TOC) concentrations decreased within 100 days. Ammonia concentrations in anaerobic lysimeters during the methanogenic phase increased by an amount four times greater than those in the acidic phase. A large change of ammonia was not observed from the aerobic lysimeters. Among 8 metals (Al, As,Cu,Cr, Fe, Pb, Mn and Zn), average concentrations of As, Fe, Mn and Zn in the anaerobic lysimeters were significantly greater than those of the aerobic lysimeters. In contrast, greater concentrations of Al, Cu,Cr and Pb were found in leachate from the aerobic lysimeters. Periods of time required for 20 % settlement for the aerobic and anaerobic lysimeters were 1 and 2 years, respectively.

Ritzkowski et al. (2006) described the fundamental processes and implications of in situ landfill aeration. By means of comprehensive laboratory-scale investigation in Landfill-Simulation-Reactors (LSRs), the significant potential of in situ aeration processes with respect to reduced leachate concentrations, as well as increased carbon degradation were demonstrated. During full-scale landfill aeration, significant changes in ambient conditions, increased settlements and temperatures, as well as significantly accelerated carbon conversion were observed. By conducting these studies, two major results were observed. The time period of uncontrolled difuse LFG emissions, as they would occur under anaerobic landfill conditions, can be shortened significantly. In addition, the off-gas composition changed, resulting in very low methane concentrations and elevated carbon-dioxide concentrations.

Moreover, a field study was carried out at two landfill sites in Georgia, USA. The first site (Columbia Country Landfill) was installed within a 6.5 ha portion of landfill near Augusta, Georgia and operated for approximately 21 months. The second site (Live Oak Landfill), was conducted at a larger landfill site in North-Central Georgia, which was operated for nine months. This 1 ha landfill cell contained approximately 57 000 m^3 of waste at an average depth of 9 m. Both landfills were converted from anaerobic to aerobic by air injection system consisting of electric blower (compressor) and piping. The analyses of vapor samples, leachate chemistry, biological activity and inspection of waste samples confirmed that simple air injection into a landfill increased waste stabilization by more than 50% and reduced leachate organic strength by up to 70% and leachate volumes by more than 80%. Waste settlement over the trial period of 9-18 months was also noted to increase by an additional 9-10 % (Read et al., 2001a, and b).

The various research projects and trial cells create a confusing picture, where some results remain unconfirmed. Considerable further research is required to obtain the future of aerobic landfill techniques. So far, all field research has taken place using existing landfill sites, so that many of the sites that are run as full-scale aerobic landfills are using waste that has been anaerobic for some time. There are questions yet to be answered about the behaviour of waste that has never been anaerobic. Lysimeter studies tend to include this possibility, but conlusions drawn from full-scale studies cannot be absolute until full scale studies are undertaken using new waste (Rich et al., 2007).

Because of higher reaction rates, aerobic biodegradation is faster process than anaerobic biodegradation. The following benefits have been observed in aerobic bioreactor landfills (Hudgins and Green, 1999);

- Faster waste and leachate stabilization
- Increased rate of landfill settlement
- Reduction of methane generation by 50-90%
- Capability of reducing leachate volumes by up to 100% due to evaporation
- Potential for landfill mining and sustainability
- Reduction of environmental liabilities

Hybrid Bioreactors (Aerobic-Anaerobic). International interest and implementation of aerobic bioreactor landfill technology is increasing. The use of this technology in Japan has been developed independently from the United States due to the particular conditions of Japan’s geography and climate. Precipitation in Japan is high with an annual average precipitation of 1750 mm, leading to the contamination of surface and groundwater. Therefore, the semi-aerobic landfill approach known as the “Fukuoka Method” was developed in cooperation between Fukuoka University and Fukuoka City and currently used as a standard type of landfill in Japan (Hanashima, 1999). This type is also suited to rainy Asian area in which the leachate control is a significant issue. Currently, it is extensively used in Malaysia and Iran. Semi-aerobic landfill is an attempt to lay the leachate collection pipe, comprising the perforated main and branch pipes and gravel, at the bottom of the landfill to discharge leachate out of the landfill as quickly possible. This prevents leachate from penetrating into the groundwater by removing leachate remaining from the bottom of the landfill. The temperature differential between the interior landfill (high temperatures) and the outside air temperature (lower relative temperatures) produces a ‘chimney’ effect, where air is drawn into the pipes and circulated throughout the waste mass. As a result, a semi-aerobic landfill type enhances the aerobic biodegradation of organic substance in landfilled municipal solid waste, consequently reduce the generation of methane and offensive odor, and the pollution caused by leachate (Higuchi, 2003)

The hybrid bioreactor, as the name implies, seeks to accelerate waste degradation by combining attributes of the aerobic and anaerobic bioreactors to rapidly degrade organics in the upper sections of the landfill and collect gas from lower sections. Figure 2.8 indicates the design and operational features of hybrid bioreactors. Operation as a hybrid results in the earlier onset of methanogenesis compared to aerobic landfills. The initial phase of aerobic treatment moves the waste body quickly through the acid phase and prepares it for the anaerobic methanogenic phase. The principle advantage of the hybrid approach is that it combines the operational simplicity of the anaerobic process with the treatment efficiency of the aerobic process. Added benefits include an expanded potential for destruction of volatile organic compounds (VOCs), hazardous air pollutants (HAPs) and non-methane organic compounds (NMOCs) in the waste mass. (http://www.wm.com/WM/environmental/Bioreactor/index.asp)

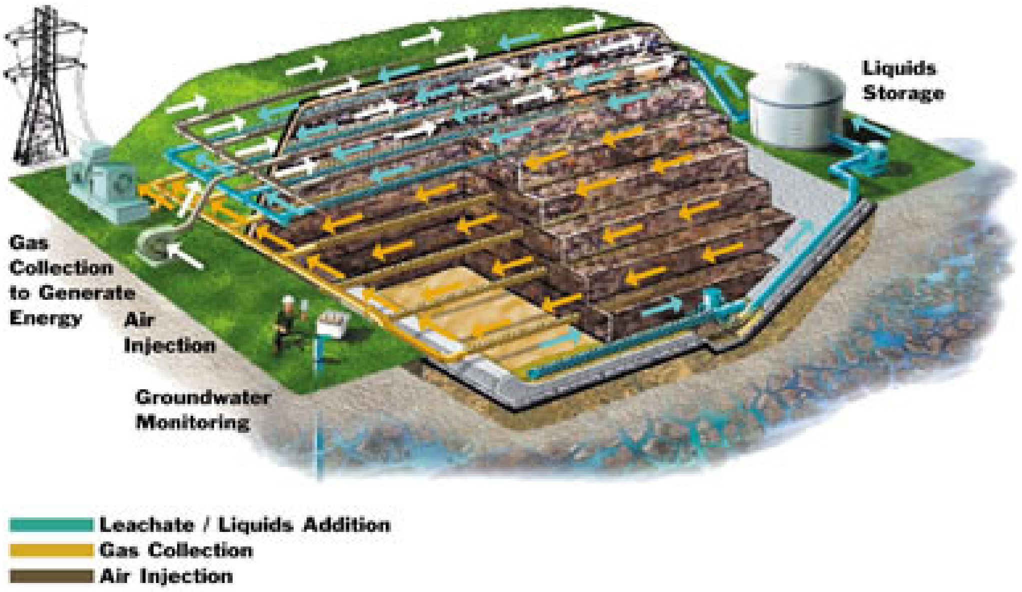


Figure 2.8. The design and operational features of hybrid bioreactors (http://www.wm.com/wm/environmental/bioreactor/bioreactorbrochure.pdf)

In Germany, a new landfill concept, aerobic biological pre-treatment of MSW has been carried out to lessen the overall waste mass, increase landfill densities, improve leachate quality (Müller et al., 2001). Pre-treatment is a landfill process in which shredded waste is subjected to forced aeration for a determined time and then allowed to go anaerobic stabilization by turning off. The goal of pre-treatment is to create a landfill without or with very little requirement for after-care, resulting in negligible gas-leachate emissions. On that basis, several works have been made to understand long term fate of mechanical-biological pretreated wastes (Lorber et.al., 2001; Müller et al., 2001; Scheelhaase , 2001). Scheelhaase (2001) reported that depending on duration, degradation rates up to 80 % of organic dried solid matter are possible. The organic load contained in the leachate of pretreated residual waste can be reduced by more than 90 %. Also, it is possible to reduce the gas production and the gas emission of landfills by 90 %.

As a result, bioreactor technology (anaerobic or aerobic) has received much more attention due to its potential for addressing landfill environmental issues more cost-effectively. Table 2.5 compares conventional landfills to anaerobic and aerobic bioreactor landfills.

Table 2.5. Comparison of bioreactor landfills (Campman and Yates, 2003).

	Conventional Landfill	**Anaerobic Bioreactor**	**Aerobic Bioreactor**
Typical settlement after:			
2 years	2-5%	10-15%	20-25%
10 years	15%	20-25%	20-25%
Anticipated waste-stabilization time frame	30-100 years	10-15 years	2-4 years
Methane generation rate	Based case	Two times base case	10-50% base case
Liquid storage capacity utilized in waste mass	none	0.14-0.29 m^3/ m^3	0.14-0.29 m^3/ m^3
Liquid evaporation	Negligible	Negligible	50-80%
Average capital cost	Low	Medium	High
Average O&M cost	Low	Medium	High
Average closure-postclosure cost	High	Medium	Low

In conventional landfills, the stabilization process takes such a long time due to the fact that the waste material has been essentially entombed in the landfill so that substantially no oxygen and moisture is introduced into the landfill. Initial waste degradation that does take place is primarily anaerobic (without oxygen), which produces harmful and objectionable by-products, such as methane gas. Although the "dry-tomb" approach is an attempt at reducing potentially polluting emissions from a landfill, this approach is a temporary solution (Read et al., 2001a). Aerobic landfill offers the potential to achieve the same waste stabilization in two or four years that conventional landfills require decades or longer to reach. On the other hand, aerobic bioreactor landfills are much more operationally intense than anaerobic bioreactor landfills. Weathers et al., (2001) determined that additional power required to inject air into an aerobic bioreactor was 12 times higher than the power required to extract LFG from an anaerobic bioreactor. However, it was estimated that the aerobic landfill approach provides potentially significant saving for many landfills when it was compared with the costs of expensive site cleanups, methane gas and leachate management closure and post-closuse (reduction in landfill gas generation) and the risk associated with landfill operations. The waste mass density in a bioreactor landfill is typically higher than in a conventional landfill due to the higher moisture content and increased consolidation of the waste mass. Conventional landfill settlement is typically around 10% of landfill height and generally occurs over a number of years as the waste decomposes. On the other hand, typical anaerobic and aerobic bioreactors can be expected to generate between 20% and 25% settlement. However, aerobic bioreactors might achieve this settlement within two to four years, while anaerobic bioreactors might require five to 10 years (Campman and Yates, 2003).

2.2 Landfill Stabilization

Solid wastes deposited in landfills decompose by a combination of chemical, physical and biological processes. These processes include, biological decomposition of degradable material by either aerobic or anaerobic processes, chemical oxidation-reduction of waste compounds, diffusion and transport of gases, liquid hydraulic transport, dissolution and transport of organic and inorganic constituents by leaching liquids, movement of dissolved constituents by concentration gradients, uneven settlement caused by consolidation of material into void spaces (Esteves, 1981). Stabilization has been described as finding a balance between the residual contaminant load and the attenuation ability of the environment (Hall et al., 2004). Assesment of the length of time required to reach this balance for some contaminants estimate in centuries rather than decades. The significance and longevity of these processes are determined by climatogical conditions, operational variables and management options (Pohland et al., 1993).

2.2.1 Biochemistry and Microbiology of Landfill Stabilization

Waste degradation in landfills is a process that requires coordinated activity of several groups of bacteria. The establishment and maintenance of a balance among all microorganisms is crucial for the efficient waste stabilization. Most of the microorganism in the landfill use organic compounds and chemical pathways to generate energy are termed chemoorganotrophs (Blackall and Silvey, 1994). As redox reactions tend to produce more energy than other types of reactions, microorganisms, which utilize these reactions, flourish within the landfill. During such reactions microorganisms use enzymes and other mechanisms to enhance the rate of such reactions and to some extent influence the point of equilibrium. As energy is released, microorganisms utilize some of this energy internally in the form of adenosine tri-phosphate (ATP), an intracellular compound used for further metabolism and reproduction. Like all chemical reactions, microorganisms are bound by the principles of thermodynamics. This, and the fact that they derive their energy from chemical reactions, is strongly reflected in typical landfill degradation behavior (Swarbrick, 2001).

Both aerobic and anaerobic processes take place in landfills. Aerobic digestion of waste is the natural biological degradation and purification process in which bacteria that thrive in oxygen-rich environments break down and digest the waste. During this oxidation process, pollutants-mainly carbohyrates, proteins and lipids- are broken down into carbon dioxide (CO_2), water (H_2O), nitrates, sulphates and stabilized humus remaining. By optimising the oxygen supply -with so-called aerators- the process can be significantly accelerated. Aerobic bacteria 'demand' oxygen to decompose dissolved pollutants. Large amounts of pollutants require large quantities of bacteria, hence the demand for oxygen will be high.

Aerobic bacteria are very efficient in breaking down waste products. As a result, aerobic treatment usually yields better effluent quality than that obtained in anaerobic processes. The aerobic pathway (Figure 2.9) also releases a substantial amount of energy. A significant fraction thereof is used by the micro-organisms for synthesis and growth of new micro-organisms (http://water.me.vccs.edu/courses/ENV149/env149_lessons.htm)

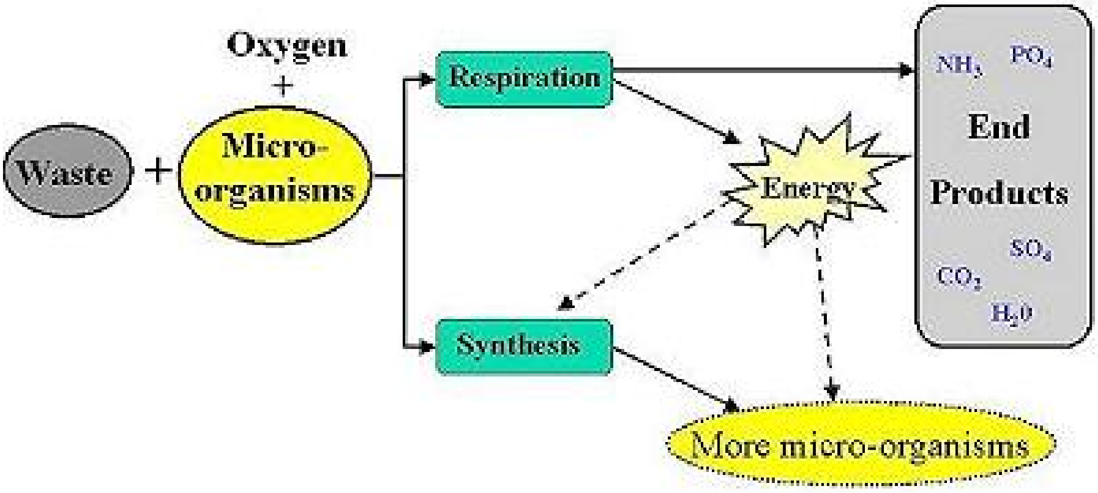


Figure 2.9. Aerobic pathway (http://water.me.vccs.edu/courses/ENV149 /env149_lessons .htm)

Waste decomposition processes in landfills proceed under anaerobic conditions after a short duration of aerobic conditions. Therefore, landfill sites are viewed as an anaerobic filters and the fundamentals and principles of anaerobic treatment are applicable to the landfills as well. Anaerobic decomposition is a multistage biochemical process that can stabilize complex organic compounds. According to many researchers, these stages change between two and nine steps (McCarty, 1966; Massey and Pohland, 1978;

Christensen and Kjeldsen, 1989; Pohland, 1992). However, a four-stage process involving hydrolysis, acidogenesis, acetogenesis and methanogenesis is used widely. Figure 2.10 illustrates four stages of anaerobic decomposition.

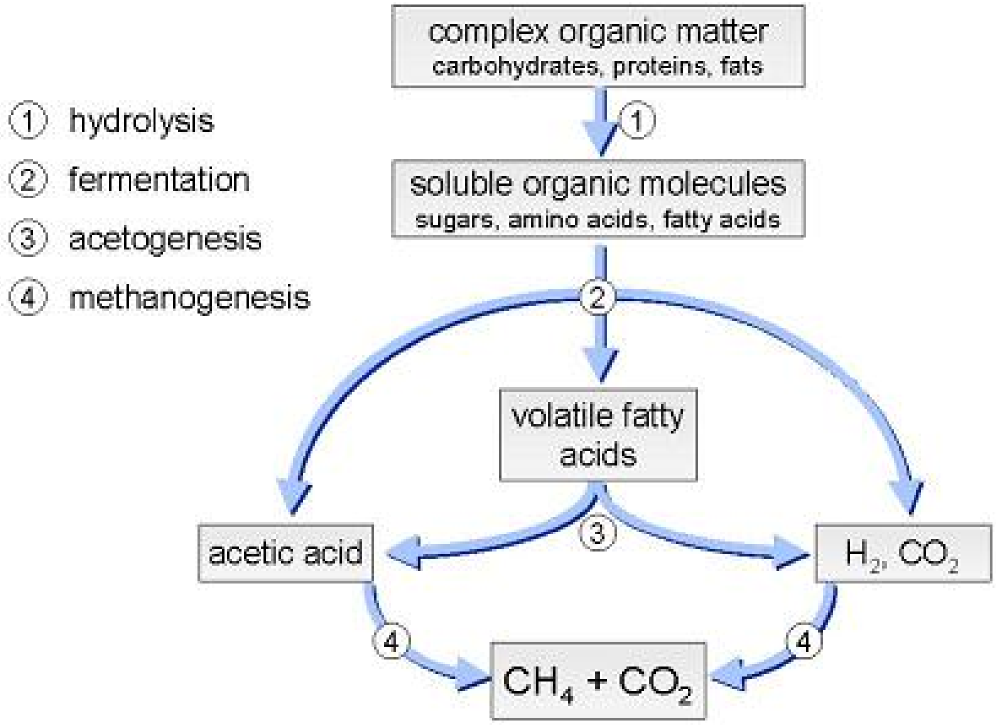


Figure 2.10. Anaerobic pathway (http://water.me.vccs.edu/courses /ENV149/env149 _lessons. htm)

In the first stage, complex organics such as cellulose, proteins, lipids and carbohydrates are hydrolyzed to dissolved organics, primarily sugars, alcohols, aminoacids and higher fatty acids. This is accomplished by extracellular enzymes of facultative anaerobic bacteria. In the second stage, hydrolyzed soluble organic compounds are fermented by acidogenesis into volatile organic acids, carbon dioxide and hydrogen gas. The third stage is the oxidation step of alcohols and volatile acids longer than two carbons to acetic acid, carbon dioxide and hydrogen. This stage is accomplished by obligate hydrogen (H_2) producing acetogenic bacteria. As the final stage, it comprises the conversion of the product of the previous steps into the final products of anaerobic decomposition that are methane and carbon dioxide by specific group of microorganism called as methanogenesis (Kızılgün, 1996). Three group of methanogenic bacteria provide methane generation; methane and carbon dioxide production from acetic acid by aceticlastic bacteria, reduction of carbon dioxide to methane by carbon dioxide reducing methanogens and a final group of bacteria that utilize formic acid and methanol to produce methane (Onay, 1995).

2.2.2 Phases of Landfill Stabilization

There are many investigations to characterize changes in landfills in term of different phases of waste decomposition (Farquhar and Rovers, 1973; Barlaz et al., 1990; Pohland et al., 1993). Pohland (1993) described refuse decomposition in five phases; initial adjustment, transition, acid formation, methane fermentation and final maturation.

Initial Adjustment Phase begins with the placement of waste into the landfill. Wastes are decomposed under aerobic conditions because a certain amount of air enters the landfill. In this phase, the low moisture content of the refuse limits microbial activity and leachate and gas production. In the Transition Phase, leachate generation is observed when the field capacity is exceeded. The primary electron acceptor shifts from oxygen to nitrate and sulfate and then to carbon dioxide. Intermediate products such as the volatile organic acids first appear in the leachate. Acid Formation Phase is the period when significant amount of intermediary volatile organic acids are produced by the continuing hdyrolysis and fermentation of waste and leachate constituents. The leachate pH decreases as a result of release of organic acid followed by mobilization and possible complexation of metal species. Nutrients, nitrogen and phosphorus are released from the waste and utilized for the support of biomass growth. Methane Fermentation Phase is the fourth phase in which intermediary products are converted to methane and excess carbon dioxide. The pH of leachate increases to neutral with the conversion of volatile organic acids. Oxidation-reduction potentials are at their lowest values. Removal of heavy metals from the leachate by precipitation and complexation with sulfide, hydroxide and carbonate anions proceeds. Nutrients continue to be consumed and leachate organic strength is dramatically decreased in correspondence with increases in gas production. In the Final Maturation Phase, active biological stabilization of readily available organic constituents in the waste and leachate has been completed. Only refractory organics remains in refuse. Nutrients may become limiting and gas production decreases. Oxygen and oxidized species may slowly reappear with a corresponding increase in oxidation-reduction potential.

Certain indicator parameters exist that are capable of being used to detect and describe the presence, intensity and longevity of each phase of landfill stabilization (Pohland and Harper, 1985). The concentration of volatile organic acids in leachate is an indication of the type and degree of waste conversion as well as the potential amount of methane and carbon dioxide that may be produced. Chemical oxygen demand (COD) and five-day biochemical oxygen demand (BOD_5) are chemical and biological parameters, respectively, and are assessed as an indication of the relative biodegradability of the waste substrate (Pohland and Harper, 1985). The variation in volatile organic acid concentrations is closely related to that of COD and BOD_5 because during the Acid Formation Phase, the majority of the COD and BOD_5 is due primarily to the presence of high concentrations of volatile organic acids. Leachate nitrogen and phosphorous concentrations are measured and indicate the availability of these principal nutrients to the anaerobic system. Oxidation-reduction potential and pH are physical and chemical parameters and are reflective of oxidation-reduction and acid base conditions, respectively. Other parameters include leachate alkalinity (buffer capacity), heavy metal concentration (potential inhibitory effects), conductivity (ionic strength/ activity), chloride concentration (constituent migration potential), nitrates and sulfates (oxidizing potential), and the presence of bacteria and or viruses(health hazards). The intensity of these parameters will vary according to the prevailing phase of landfill stabilization and the manifestation of waste conversion. In addition to variations with the microbially- mediated stabilization processess, these parameters will be influenced by the amount of moisture entering the landfill, as dilution effects become more pronounced with increasing moisture flux. (Pohland et al., 1993)

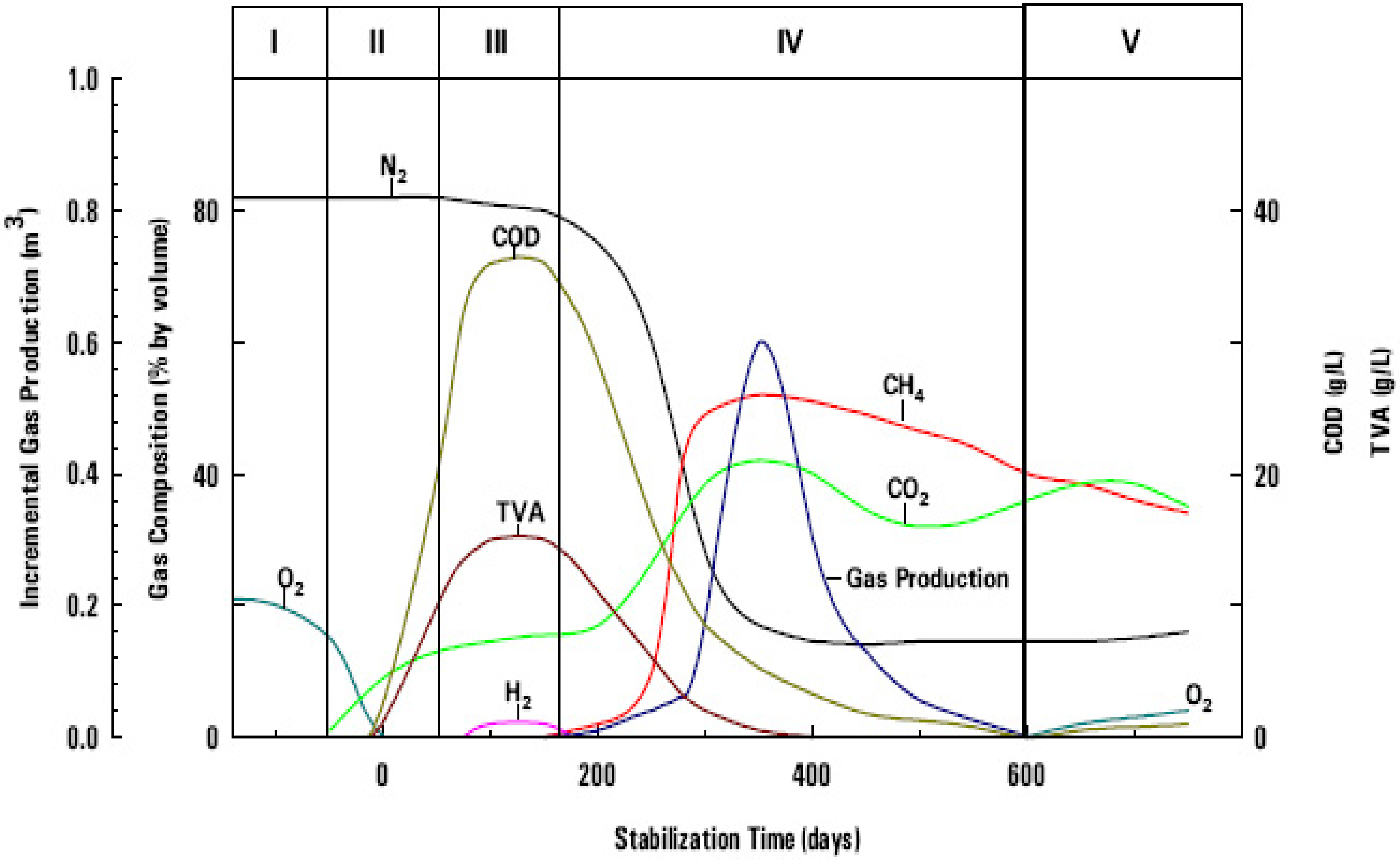


Figure 2.11 Waste stabilization phases (Kim 2001)

2.2.3 Factors Affecting Landfill Stabilization

Environmental factors such as aeration, temperature, pH, nutrients, moisture, presence of toxic substances and input solid waste characteristics affect microbially-mediated waste stabilization in landfills.

2.2.3.1. Aeration. In anaerobic landfills, methanogens require the absence of oxygen with a redox potential of below -330 mV (Christensen and Kjeldsen, 1989). In aerobic landfills, on the other hand, the proper oxygen must be injected in landfills in order to prevent anaerobic conditions and adjust temperature and moisture content of mass. Preferably, compressed air is the source of oxygen to promote and maintain primarily aerobic degradation (Read et al., 2001a). Aeration plays a critical role in landfills. The removing of excess moisture from the wet materials and controlling of the landfill temperature are made by aeration. The aeration rate of an aerobic landfills depends on the nature and quatity of waste. Therefore, the supply of proper aeration rate for landfills is very difficult. A wide range of aeration rates for solid waste have been reported in the literature (Haug 1993; Cossu et.al., 2003; Bernreuter and Stessel, 1999) and summarized in Table 2.6.

Table 2.6. Literature review of aeration rates in aerobic landfills

Reference	**Aeration rates**
Borglin et al., (2004)	0.04 L/min/kg waste
Ishigaki et al., (2003)	0.8 L/min/kg waste
Cossu et al., (2003)	0.17 L/min/kg waste
Kim and Yang (2002)	0.003 L/min/kg waste
Smith et al., (2000)	0.0002 L/min/kg waste
Hanashima (1999)	4.2 L/min/m^3 waste
Bernreuter and Stessel (1999)	0.5 L/min/kg waste
Keener et al., (1997a,b)	0.35-0.97 L/min/kg waste

Theoretically, the amount of oxygen required is determined by the amount of carbon to be oxidized. However, it would be impossible to arrive at a precise determination of the oxygen requirement on the basis of the carbon content of the waste since an unknown fraction of the carbon is converted into bacterial cellular matter and another unknown fraction is so refractory in nature that its remains inaccessible to the microbes. There is a general consensus that an airflow providing an outlet CO_2 concentration of about 15% is sufficient for the aerobic decomposition of solid wastes (Binner et al., 2003).

2.2.3.2. Temperature. Temperature is a key factor for successful landfill stabilization of organic matter and influences the types of bacteria in landfills. Three temperature ranges are defined for anaerobic decomposition: psychrophilic (below 20 °C), mesophilic (20-40 °C) and thermophilic (50-70 °C). The optimum temperature range for mesophilic anaerobic digestion reported by McCarty (1963a and b) is 30-37 °C (Esteves, 1981). The optimum temperature for thermophilic refuse decomposition reported by Pfeffer (1974) is at least 60 °C (Barlaz, Ham and Schaefer, 1990). Hartz et al. (1982) investigated the impact of temperature ranges of 21 °C to 48 °C on the rate of methane production and the optimum temperature was found to be 41 °C, with methane evolution ceasing between 48°C and 55°C.

Futhermore, temperature within the landfill mass is a critical element in promoting and maintaining the aerobic degradation. It was stated that the optimum temperatures in the aerobic landfills were between 35°C and 55°C (Hudgins and Harper, 1999). Previous field demonstrations of aerobic landfill treatments have shown temperature increases up to 60°C (Hudgins and March, 1998). Aerobic reactions are exothermic reactions that increase the temperatures of the environment. Excess temperature may disrupt or cease biological activities in the landfills. Waste temperature can be controlled by changing the rate of air and liquid addition (Read et al., 2001a). The amount of heat energy generated by anaerobic decomposition process is small compared to aerobic degradation.

2.2.3.3. pH and Alkalinity**.** pH is an important parameter as it directly effects the growth of microorganisms and the solubility of substances. It is generally accepted that the optimum pH for anaerobic decomposition ranges between 6.4 and 7.6 (Anderson and Yang, 1992). Farquhar and Rovers (1973) reported that optimal pH for methane production and that reduction in pH occurs in response to an inhibition of methane with a resultant accumulation of organic acids. The pH of an anaerobic system is a function of volatile organic acids, alkalinity concentrations and the partial pressure of carbon dioxide evolved during stabilization. Therefore, a sufficient amount of alkalinity provides a good safety margin against sudden increase in the concentration of volatile acids and pH fluctuations. The total alkalinity of 1000-5000 mg/L as $CaCO_3$ is suitable for decomposition of refuse (Tchobanoglous and Burton, 1979). Farquhar and Rover (1973) reported that an alkalinity in excess of 2000 mg/L as $CaCO_3$ is considered optimum.

pH is also important for the aerobic decomposition. The pH level usually drops at the starting of aerobic landfills. The pH drop is the result of the formation of volatile fatty acids. When the acids are utilized by microorganisms as substrates, the pH level begins to rise. Aerobic reactions may occur in the pH range of 3-11, but better results are obtained in the pH range of 5-9 (Chefetz et al., 1996). The pH of the aerobic landfills is more alkaline than the pH from anaerobic landfills due to CO_2 stripping by air; a decrease in CO_2 leads to a decrease in carbonic acid (H_2CO_3) and bicarbonate ion concentrations (HCO_3^-) consuming H^+ ions (Kim, 2005).

2.2.3.4. Nutrients. Bacteria in anaerobic and aerobic processes require a broad spectrum of nutrients for growth and cell maintaince, including carbon, nitrogen, phosphorus, sulphur, calcium, magnesium, potassium, sodium, organic nutrients such as amino acids and vitamins and trace metals such as iron, nickel, cobalt, molybdenum and selenium (Barnes and Fitzgerald, 1987). While nitrogen and phosphorus are required in larger amounts, only trace quantities of other nutrients are required for bacterial cell maintenance and synthesis (Rachdawong, 1994). The nutrient requirement of system is described by COD:N:P ratio. The optimal ratio evaluated by McCarty (1964a and b) is 100:0.44:0.08 for anaerobic processes and phosphorous is the nutrient most likely limiting the decomposition (Christensen and Kjeldsen,1989). On the other hand, in aerobic processes, it has been found that a preferred concentration ratio of carbon to nitrogen in the range of about 20:1-50:1 is desired (Read et al., 2001a).

2.2.3.5. Moisture Content. Moisture content is considered one of the most important parameter in solid waste decomposition and gas production because it provides a medium for transporting nutrients and bacteria throughout the landfill (McBean, Rovers and Farquhar, 1995). Farquhar and Rovers (1973) reported that the gas production increases at moisture contents from 60% to 80% wet weight, whereas, it ceased at moisture content ranging from 30% and 40% wet weight. Barlaz and coworkers (1987) reported that 55% moisture cannot assure methane production.

The capability to deliver moisture to indivual zones within the landfill is also an important control mechanism for the aerobic degradation. Moisture content of generally about 40% is essenstial for rapid aerobic degradation. Microbial activity, and, therefore, degradation, slows by several orders of magnitude below a moisture content of around 40%. Below 20%, degradation essentially ceases. It was determined that an ideal moisture content in the landfill for aerobic degradation is about 60% (Read et al., 2001a and b). This moisture content allows for adequate oxygen diffusion through the waste material to support the rapid aerobic degradation. If the moisture content is too low, the landfill is dry and aerobic decomposition will cease. Conversely, if the moisture content is to high, diffusion of oxygen is hampered thereby limiting aerobic activity.

2.2.3.6. Toxic Substances. The microbial processes in landfills are adversely affected by the presence of toxic substances including high concentration of ammonia nitrogen, sulphides, heavy metals, toxic organic constituents and excess volatile organic acids

Ammonia formed in anaerobic processes from degradation of wastes containing proteins and urea. Ammonia may be present either in the form of ammonium ion (NH_4^+) at pH less than 7.2 or as ammonia (NH_3) at higher pH values. Ammonia is inhibitory at much lower concentration than the ammonium ion. Although the presence of ammonia nitrogen is beneficial between the concentrations of 50-200 mg/L on methanogens. Its inhibitory effects have been observed at about 1500-2000 mg/L especially at high pH values and concentrations above 3000 mg/L were toxic regardless of pH (Kızılgün,1996). Sulfides are produced during anaerobic decomposition from reduction of sulfates and other sulfur containing inorganic compounds. Sulfides may exist in a soluble, insoluble form or gaseous hydrogen sulfides. Heavy metal sulfides are insoluble and precipate from solution to lessen their toxic effects (Esteves, 1981). The sulfide threshold value ranges from 200-1500 mg/L (Pohland, 1992).

Heavy metals can be inhibitory to microbial life above threshold concentrations even though trace amounts of metals are necessary for microorganisms. The presence of sulphides, carbonates and hydroxides in the anaerobic processes decreases the toxic effect of heavy metals on methanogens depending on the system pH. Pohland (1992) reported the list of heavy metals according to the order of its decreasing toxicity; Ni>Ca>Pb>Cr>Zn and iron considered more beneficial than detrimental because of its mediating effects on sulfide toxicity. Alkali and alkali-earth metals such as sodium, potassium, calcium and magnesium have toxic effects on anaerobic systems above certain concentrations. However, the toxic effects of a particular cation present a waste may be reduced or eliminated by addition of another ion, an "antagonist", conversely, toxicity may be increased by addition of a "synergist" (Barnes and Fitzgerald, 1987). Sodium and potassium are most effective antagonist and when added will decrease the toxicity caused by other cations.

The accumulation of volatile organic acids may also inhibit the methanogenic microbial growth. While acetic acid is the least toxic, propionic acid is the most toxic volatile fatty acid (Pohland, 1992).

2.2.3.7. Input Solid Waste Characteristics. Refuse composition is considered to be important because the nature of waste organic fraction influences the degradation of waste. In particular, the presence of substances which are toxic to bacterial flora may slow down or inhibit biological degradation processes (Gürsoy, 1998). Moreover, particle size of waste influences decomposition rate. Ham and Bookter (1982) investigated the effect of shredding on the decomposition process and they reported that the shredding of refuse increases the rate of decomposition and leads more quickly to methane production.

2.2.4. Landfill Attenuation Mechanisms

Attenuation is a combination of chemical, physical and biological processes that causes a temporary or permanent decrease in the concentrations of many contaminants of waste. These processes include; diffusion and transport of gasses, liquid hydraulic transport, dissolution and transport of organic and inorganic constituents by leaching liquids, chemical oxidation-reduction, adsorption, ion exchange, precipitation and complexation of waste compounds, biological decomposition of degradable material by either aerobic or anaerobic processes (Esteves, 1981; McBean et.al., 1995; Quasim and Chiang, 1994).

2.2.4.1. Carbon. Under anaerobic conditions, the carbonaceous organic matter is decomposed to produce organic acids, carbon dioxide, methane and many other complex organic compounds. On the other hand, under aerobic conditions the carbonaceous organic matter, ammonia, sulfide, phosphorus, iron and manganese are converted to carbon dioxide, nitrate, sulfate, phosphate and oxidized states of iron and manganese, respectively. The principal use of anaerobic or aerobic wastewater treatment processes is to reduce concentrations of organic compounds typically found in wastewater. In a similar manner, the fundamentals and principles of anaerobic and aerobic treatment are applicable to the landfills as well. Landfilled wastes are dominated by organic material comprising (typically) of 50% cellulose, 15 % lignin, 10 % hemicellulose, 5 % protein as well as starch, pectin, and other soluble sugars (Barlaz, 1992). Cellulose is the most important carbon source for mathanogenesis in landfills, however it is not an easily biodegradable material under anaerobic conditions. In fact, cellulose and hemicellulose whose half-lifes are about 15 years would contribute to 90 % of total methane produced (Swarbrick, 2001). Hydrolysis of these complex organics in the presence of oxygen enhance biodegradation rate and convert to organic carbon in waste mass to mostly carbon dioxide and water, with a stabilized humus remaining. Waste decomposition takes place within a few years under aerobic and controlled conditions instead of several decades (Hudgins and Harper, 1999).

2.2.4.2. Nitrogen. After carbon, nitrogen is another major constituent in leachate and can pollute soil and water. Because ammonia-nitrogen persists even after the organic fraction of the waste is stabilized, and because of its toxic nature, it is likely that ammonia-nitrogen will determine when the landfill is biologically stable and when post-closure monitoring may end (Kjeldsen et al., 2002, Robinson and Maris, 1985). Thus an understanding of the fate of nitrogen in bioreactor landfills is critical to a successful and economic operation (Berge 2006). Figure 2.12 illustrates the potential nitrogen transformation and/or removal pathways that may occur in bioreactor landfills. The heterogeneous nature of solid waste

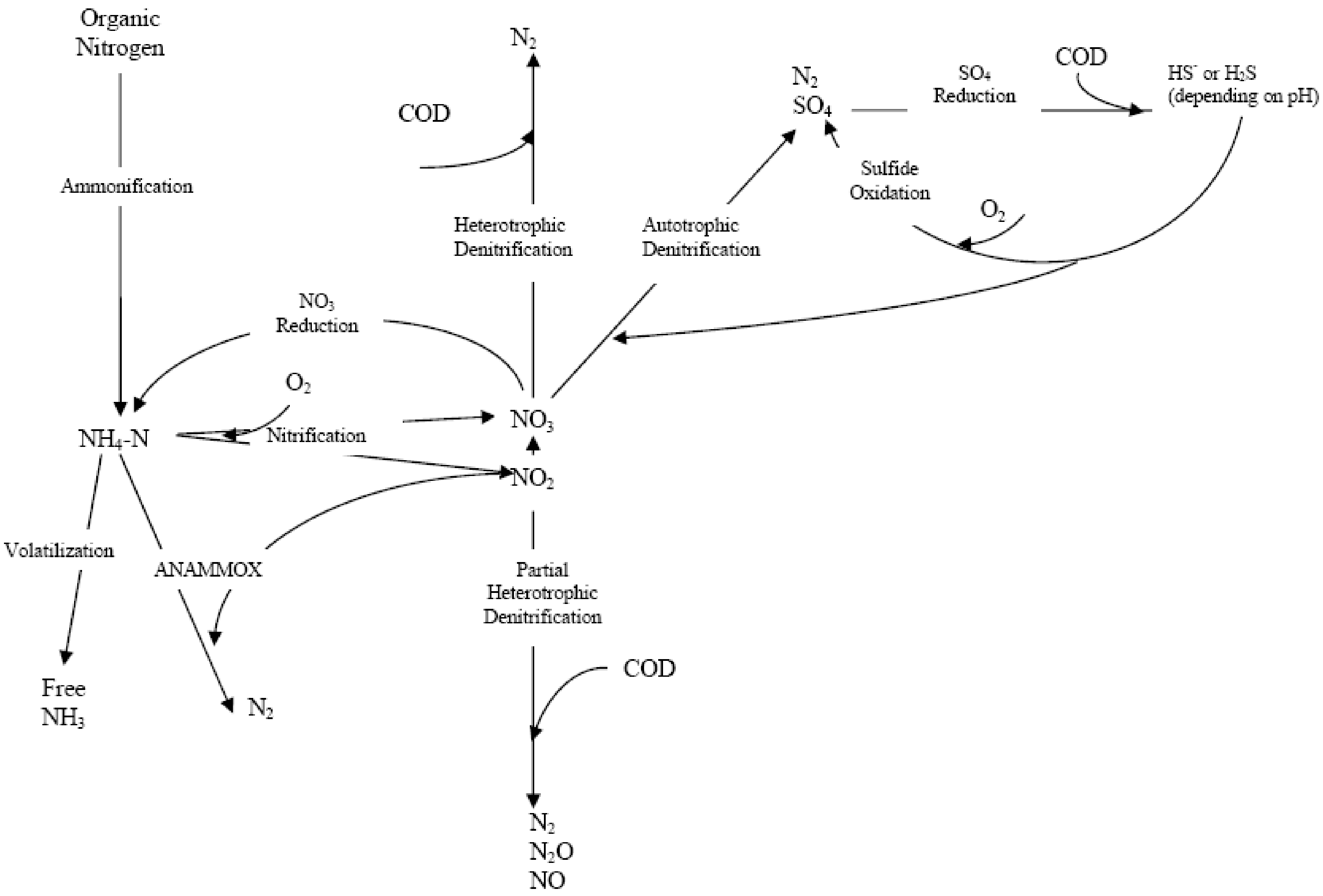


Figure 2.12. The potential pathways of nitrogen transformation and/or removal in bioreactor landfills (Berge 20006).

complicates the nitrogen cycle in bioreactor landfills. Ammonification, sorption, volatilization, nitrification, denitrification, anaerobic ammonium oxidation (ANAMMOX) and nitrate reduction are processes for transformation or removal of nitrogen and may all occur in bioreactor landfills.

Ammonification is a two-step process consisting of the enzymatic hydrolysis of proteins by aerobic and anaerobic microorganisms releasing amino acids and the subsequent deamination or fermentation (depending on aerobic vs. anaerobic conditions) of the acids to carbon dioxide, ammonia-nitrogen, and volatile fatty acids (Burton and Watson-Craik, 1998). Under anaerobic conditions, nitrogen transformed from organic nitrogen to ammonia. Protein fractions of biodegradable wastes release ammonia nitrogen and they may accumulate in leachate to concentrations of 1000-3000 mg/L in anaerobic landfills. Therefore, the toxicity of the leachate increases, potentially inhibiting the degradation process and necessitating leachate treatment before ultimate disposal to protect receiving waters (Burton and Watson-Craik, 1998, 2001).

Under aerobic conditions, the ammonia-nitrogen is dissolved in the leachate and is ready to be transformed and/or removed via volatilization, sorption, or biological processes. In landfills in which air is purposely added, nitrification can be a significant nitrogen removal pathway. Nitrification is a two-step aerobic process in which ammonia-nitrogen/ammonium is microbially oxidized to nitrite and nitrate via obligate aerobe, autotrophic, chemolithotrophic microorganisms named as nitrifying bacteria (*Nitrobacter and Nitrosomonas*). In anoxic conditions, denitrification processes will potentially reduce nitrate and nitrite to nitrogen gas. Understanding of the biological and chemical mechanisms associated with coupled nitrification and denitrification within the waste mass is essential to maximize the potential of these processes. A related study was conducted by Onay (1995) to demonstrate in situ removal of nitrogenous compounds in laboratory-scale simulated landfill units under leachate recirculation. A three-component landfill system including anoxic, anaerobic and aerobic zones was simulated for nitrogen conversion. The sources of carbon and nitrate necessary for denitrification was supplied by utilizing leachate recycle to carry the residual C and N from the anaerobic zone into the aerobic zone, and subsequently to the anoxic zone. Results from the three simulated operational stages of methanogenesis, nitrification and denitrification indicated that the rate of nitrate removal was rapid and the efficiency of nitrogen conversion was 95 %.

Biological oxidation of ammonia-nitrogen may also occur under anaerobic conditions and is termed the ANAMMOX process (ANaerobic AMMonium OXidation). There has been little research concerning ANAMMOX in solid waste environments, however, studies conducted in wastewater have shown that ANAMMOX readily occurs (Hao et al., 2002; Jetten et al., 1998; Jetten et al., 2001; Schmidt et al., 2003). The growth rates of the ANAMMOX bacteria are extremely slow, thus ammonia-nitrogen removal is slow as well. It is questionable whether or not the ANAMMOX microorganisms will be able to compete with denitrifiers for nitrate and nitrite within landfills (Burton and Watson-Craik, 1998). Removal rates have been shown to be less than half that of aerobic nitrification (Ye and Thomas, 2001).

On the other hand, dissimilatory nitrate reduction to ammonium (DNRA) in anaerobic or anoxic environments may also occur in landfills. DNRA is favored over denitrification in anaerobic and anoxic environments in environments with a high COD to nitrate ratio because in an electron acceptor limiting environment it is more advantageous for the microorganisms to metabolize nitrate to ammonium and gain eight electrons per mole of nitrate than denitrify and only gain five electrons per mole of nitrate (Tiedje, 1988). The dissimilatory nitrate reduction pathway is not desired because it results in an increase in ammonium concentration. However, this removal mechanism may be limited because of competition from the denitrifiers for nitrate. The nitrate reducing bacteria require a tenfold greater population than denitrifiers to reduce 50% of the nitrate (Price et al., 2003). Bonin (1995) reported a ratio of 1.8:1.0 denitrifiers to DRNA microbes are generally present in an environment. In landfills, there is generally adequate denitrifying populations naturally present to out-compete any DNRA capable microorganisms. Price et al. (2003) conducted laboratory studies in solid waste evaluating the denitrification capacity of the waste and found that there was no noticeable increase in ammonium due to DNRA.

2.2.4.3. Heavy Metals. There have been large number of studies in which researchers have reported metals concentrations from full-scale landfills, test cells and laboratory studies under anaerobic conditions (Flyhammar et.al, 1998; Kruempelbeck and Ehrig, 1999; Revans et al., 1999). Even though trace amounts of metals are necessary for microorganisms, they can be inhibitory to microbial life above threshold concentrations and adversely affect degradation process. Four attenuation mechanisms have been found to control heavy metal concentrations in landfill leachates: adsorption, acid-base, oxidation-reduction, precipitation/complexation reactions (Pohland et al., 1988).

Adsorption of heavy metals onto the waste is the important removal process occurring inside the landfills. However, there are limited quantitive data about heavy metal adsorption potential of domestic refuse in literature due to both the heterogeneity of received refuse and the absence of standard procedures for the determination of adsorption characteristic of specific wastes (Erses et al., 2005).

The pH is also a major determinant of the behavior of heavy metals in landfills. In general, the solubility of heavy metals is higher at $pH < 4$ than at $pH > 7$ (Watson-Craik and Sinclair, 1995). Therefore, the progress of landfill stabilization through aerobic and anaerobic degradation will significantly influence pH and associated heavy metal solubility.

The chemical environment of a sanitary landfill is typically reducing due to biologically mediated oxidation-reduction reactions and limited access to atmospheric oxygen. This condition affects heavy metal mobility in two ways. First, between the oxidized and reduced form of a metal, e.g., Fe^{+3}/Fe^{+2}, Mn^{+4}/Mn^{+2}, the reducing potentials will favor the reduced species over the oxidized several potentially significant metals such as $Mn^{+7}/ MnO_2/ Mn^{+2}$, Fe^{+3}/Fe^{+2}, $Cr^{+6}/ Cr^{+3}/ Cr^{+2}$ and Hg^{+2}/ Hg_2^{+2} will undergo redox-dependent transformation which will strongly influence their mobility and potential for migration through and from a landfill site. Secondly, the reducing conditions will facilitate reduction of sulfate to sulfide. Since sulfide is a powerful precipitant for many heavy metals, the formation of this species will provide a mechanisms by which toxic heavy metals can be immobilized, even at relatively low pH conditions (Lee, 1989).

Soluble metals precipitate as insoluble sulfides, carbonates, hydroxides, and, possibly, phosphates in the landfills (Pohland, 1991). Under anaerobic conditions, all heavy metals except chromium form extremely insoluble sulfide salts as a consequence of the very low solubilities of heavy metal sulfides (Pohland et al., 1981). Chromium solubility, in either hexavalent or trivalent state, is determined by hydroxide equilibrium (Esteves, 1981). Chromium with its low hydroxide solubility ($pK_{so} = 30.8$) would precipitate as $Cr(OH)_3$ even at pH levels as low as 5.0 since ORP conditions required to reduce chromium and permit formation of possible other complexes are not attained within the landfill environment.

The solubility of heavy metals decreases as the pH increases. Of importance to pH considerations is hydroxide and carbon dioxide, carbonate systems. For some metals, when soluble sulfide concentrations are as low as 10^{-6} molar, their solubility is controlled by the hydroxide and carbonate / bicarbonate equilibrium. This is true for metals like cadmium, copper, lead and chromium which are precipitated as carbonate and hydroxy-carbonate species ($CdCO_3$, $Cu_3(CO_3)_2(OH)_2$, $PbCO_3$ and $Cr(OH)_3$), while zinc and nickel would be least likely to precipitate in these forms. However, even at soluble sulfide concentrations of 10^{-8} molar, the control of solubility of such metals as Hg_2^{+2}, Cu^{+2}, Cd^{+2}, Pb^{+2} and Ni^{+2} will remain in the domain of the sulfide system (Pohland and Gould, 1980).

Complexation is the combination of metal ions with non-metallic compounds called ligands such as chloride, aromatic acids, amino acids. Heavy metals dissolved in aqueous systems exist as complexes and not free ions; in the case of natural waters, the ligands involved are almost exclusively water or the hydroxide ion. Leachates provide a vast array of ligands; either organic or inorganic. However, it is important to note that sulfide competes very effectively with most complexing agents so that in the presence of sulfides, metal complexation should be of little or no consequence (Esteves, 1981).

In aerobic landfills, on the other hand, researchers expected that aeration of landfill may result in increased heavy metal concentrations in leachate because of metal sulfates that are generally more soluble. For example, pK_{so} values for PbS and $PbSO_4$ are 27.6 and 7.73, respectively. However, limited studies indicated that no significant release of heavy metals under aerobic conditions was observed compared to anaerobic conditions. Bozkurt et al. (1997) developed a model to predict long-term metals release from landfills. Their model considered the oxidation of refuse, organic matter, humic substances and metal sulfide precipitates, as well as pH buffering associated with calcite dissolution. They saturation and predicted heavy metals mobilization will not occur for thousands of years. The current challenge is to verify this result experimentally.

2.2.4.4. Sulfur. Sulfur compounds are present in the waste and landfill leachate principally as soluble sulfate and precipitated sulfide forms. Figure 2.13 is a pH-Ec diagram for the sulfate- sulfide system and indicates conditions necessary to favor the presence of sulfide. Sulfides can be formed during anaerobic decomposition either from sulfur containing amino acids or by reduction of inorganic sulfur compounds (Rinzema and Lettinga, 1988). Dissimilatory microbial sulfate reduction is a process in which certain bacteria use sulfate as the electron acceptor in the oxidation of organic matter. Sulfate in which the sulfur is in the +6 oxidation state, is reduced to sulfide, in which the sulfur is in the –2 oxidation state. *Desulfovibrio* and *Desulfotomaculum* are two genera of sulfate-reducing bacteria (Middleton and Lawrence, 1977).

It is known that sulfate reduction and methane production can occur at the same environment. Biological sulfate reduction removes organic material that might otherwise be converted to methane and the production sulfide can cause the precipitation of iron, nickel and cobalt which are essential nutrients for methanogens. Sulfate reducing bacteria (SRB) have a thermodynamic advantage over the methane producing consortia. SRB will out-compete the methane-producing consortia for available substrates. Hence sulfide toxicity will be more severe for methane producers (Parkin et al.,1991). On the other hand, sulfides are required by methanogens as trace nutrients. The sulfide content of methanogens is 2.6% (Esteves, 1981).

Sulfate reducing bacteria (SRB) play an important role in the removal of heavy metals in anaerobic systems. Jalali and Baldwin (2000) reported that copper was seen to precipitate out more quickly in the presence of sulfate reducing bacteria cells than without bacteria cells. Thus, association of copper with sulfate reducing bacteria cells promotes precipitation kinetics.

When organic sulfur compounds are decomposed by bacteria the initial sulfur product is generally the reduced form, H_2S. Although a fraction of sulfide escapes in the anaerobic systems in the biogas, the majority of sulfide remains dissolved in solution as either H_2S (aq) or HS^- (McFarland and Jewell, 1989). H_2S (aq) is in equilibrium with H_2S (g) and when pH increases, H_2S (aq) is converted to HS^-. The dissolution of H_2S in water forms the following equilibrium system.

$$H_2S \leftrightarrow H^+ + HS^- \leftrightarrow 2\ H^+ + S^{-2} \tag{2.3}$$

Depending on the pH, the percentage of un-ionized H_2S drops from 90% at pH 6.0 to 50% at pH 7.0 and to 10% at pH 8.0 (Oleskiewicz and Hilton, 1985). Total dissolved sulfide concentrations (H_2S+ HS^-+ S^{-2}) of 145-200 mg S/L result in SRB and MPB inhibition in anaerobic systems (Fairweather and Barlaz, 1998). Metal-sulfide precipitation as indicated in equation 2.3 is the major factor controlling biological inhibition (Bozkurt et al., 1997).

$$Me^{+2} + S^{-2} \rightarrow MeS \tag{2.4}$$

where Me is taken as the symbol for a metal

However, to our knowledge, there are no reports on the fate of sulfur compounds in the literature for an aerobic landfill. Therefore, laboratory and field studies are required to make this evaluation.

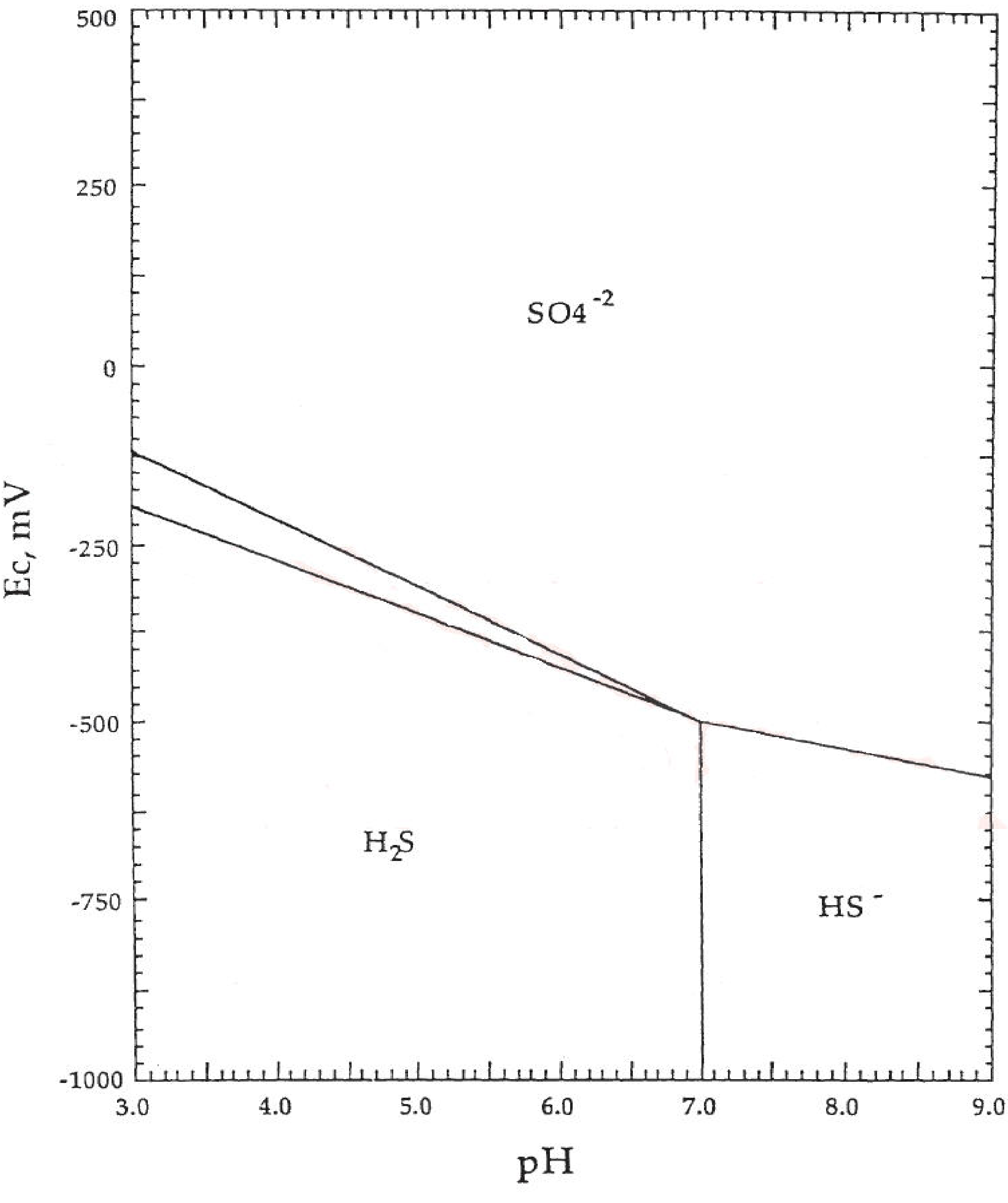


Figure 2.13. Ec-pH diagram for $SO_4^{-2}/S^0/S^{-2}$ (Esteves, 1981)

2.2.5. Thermodynamic Considerations

A better understanding of interactions emanating from sequential environments provide improved management alternatives. Complete anaerobic or aerobic digestion of complex organic matter is accomplished by many interacting groups of organisms that obtain their energy for growth and maintenance from oxidation-reduction reactions. Under anerobic conditions, the organic matter is degraded in a stepwise manner, the products of one group of organisms are substrates for subsequent reactions catalyzed by other groups. One physiological group of organism may depend on other groups for the production of its substrate, and still other groups for removal of its products.

Methane fermentation occurs by two primary mechanisms: cleavage of acetic acid to yield methane and carbon dioxide; and the reduction of carbon dioxide using hydrogen as the energy source. Approximately 70 to 73 % of the methane produced comes from acetate cleavage, and the remaining 27 to 30 % originates from carbon dioxide reduction. On the other hand, the production of methane from acetate yields only 31 kJ per mole CH_4 produced. This is barely enough energy for the degradation of adenosine triphosphate (ATP), which requires 306 kJ/mole, resulting in the slow growth of methanogens on acetate whereas the conversion of H_2 with CO_2 to CH_4 yields 135.6 kJ per mole CH_4 produced as listed in Table 2.6. Therefore, the latter reaction is energetically more favorable (Kim, 2001).

Landfill leachate contains significant levels of sulfates and ammonia, in addition to high levels of waste organic materials. The successful anaerobic treatment requires an understanding of the competition for methanogenic precursors by sulfate reducing bacteria (SRB) and nitrate reducing bacteria (NRB). Researches have shown that both sulfate and nitrate reducing bacteria presents in anaerobic systems, compete with methanogens for hydrogen and acetic acid. The reduction of sulfate to hydrogen sulfide occured with the oxidation of carbon to carbon dioxide. As presented in Table 2.6, nitrate reduction is the most energetically favorable reaction, followed by sulfate reduction and lastly, methane formation from both acetic acid cleavage and carbon dioxide reduction (Pohland et al., 1993).

Table 2.7. Redox half-reactions responsible degradation of selected organics during anaerobic treatment (Pohland et al., 1993)

	Oxidations (electron donating reactions)[a]	ΔG^0 (kJ)
Caproate ⇔ Propionate	$CH_3(CH_2)_4COO^- + 2H_2O \Leftrightarrow 2CH_3CH_2COO^- + H^+ + 2H_2$	+48.3
Caproate⇔Acetate	$CH_3(CH_2)_4COO^- + 4H_2O \Leftrightarrow 3CH_3CH_2COO^- + 2H^+ + 4H_2$	+96.7
Caproate ⇔ Butyrate + Acetate	$CH_3(CH_2)_4COO^- + 2H_2O \Leftrightarrow CH_3(CH_2)_2COO^- + CH_3COO^- + H^+ + 2H_2$	+48.4
Propionate ⇔Acetate	$CH_3CH_2COO^- + 3H_2O \Leftrightarrow CH_3COO^- + H^+ + HCO_3 + 3H_2$	+76.1
Butyrate ⇔Acetate	$CH_3CH_2CH_2COO^- + 2H_2O \Leftrightarrow 2\ CH_3COO^- + H^+ + 2H_2$	+48.1
Ethanol ⇔Acetate	$CH_3CH_2OH + H_2O \Leftrightarrow CH_3COO^- + H^+ + 2H_2$	+9.6
Lactate ⇔Acetate	$CH_3CHOHCOO^- + 2H_2O \Leftrightarrow CH_3COO^- + HCO_3^- + H^+ + 2H_2$	-4.2
Acetate ⇔Methane	$CH_3COO^- + H_2O \Leftrightarrow HCO_3^- + CH_4$	-31.0
	Reductions (electron accepting reactions)[a]	
HCO_3^- ⇔Acetate	$2HCO_3^- + 4H_2 + H^+ \Leftrightarrow CH_3COO^- + 4H_2O$	-104.6
HCO_3^- ⇔Methane	$HCO_3^- + 4H_2 + H^+ \Leftrightarrow CH_4 + 3H_2O$	-135.6
Sulfate ⇔ Sulfide	$SO_4^{2-} + 4H_2 + H^+ \Leftrightarrow HS^- + 4H_2O$	-151.9
	$CH_3COO^- + SO_4^{2-} + H^+ \Leftrightarrow 2HCO_3^- + H_2S$	-59.9
Nitrate ⇔ Ammonia	$NO_3^- + 4H_2 + 2H^+ \Leftrightarrow NH_4^+ + 3H_2O$	-599.6
	$CH_3COO^- + NO_3^- + H^+ + H_2O \Leftrightarrow 2HCO_3^- + NH_4^+$	-511.4
Nitrate ⇔Nitrogen gas	$2NO_3^- + 5H_2 + 2H^+ \Leftrightarrow N_2 + 6H_2O$	-1120.5

Note: [a]pH 7, 1 atm, 1kg/mol activity, 25°C

On the other hand, microorganisms would like to obtain as much energy from a reaction as possible; therefore, they would prefer to use oxygen as an electron acceptor when oxygen is available. Examples of different energy reactions in which glucose is the electron donor listed below, show that the energy gained from one mole of glucose varies widely, depending on the electron acceptor.

	Free Energy (kJ/mol glucose)
Aerobic oxidation:	
$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$	-2.880
Denitrification:	
$5C_6H_{12}O_6 + 24\ NO_3^- + 24H^+ \rightarrow 30\ CO_2 + 42\ H_2O + 12N_2$	-2.720
Sulfate reduction:	
$2C_6H_{12}O_6 + 6SO_4^{2-} + 9H^+ \rightarrow 12CO_2 + 12\ H_2O + 3H_2S + 3HS^-$	-492
Methanogenesis:	
$C_6H_{12}O_6 \rightarrow 3CO_2 + 3CH_4$	-428
Ethanol Fermentation:	
$C_6H_{12}O_6 \rightarrow 2CO_2 + 2CH_3CH_2OH$	-244

Obviously, the order of preference for electron acceptors based upon energy considerations alone would be oxygen, nitrate, sulfate, carbon dioxide (methanogenesis), and, finally, fermentation (Rittmann and McCarty, 2001).

3. PROBLEM DEFINITION

Up to date, several laboratory and pilot-scale investigations of different landfill concepts have been carried out to achieve sustainability by reducing long term landfill emissions. Leachate recirculation, flushing bioreactor, pre-treatment and aeration methods have evolved to obtain a low-emission landfilling alternative. Through the continued developments of these methods, the aerobic landfill concept which depends on aerobic degradation of municipal solid waste is a new perspective on waste landfilling and suitable way to minimize environmental impacts. However, high initial capital cost of aeration sytems and high operation cost throughout landfilling forced to modify the aerobic landfill concept by using limited aeration.

This study aims to evaluate an efficient and cost-effective landfill management concept by using aerobic, anaerobic and the combinations of these two processes. The attenuation mechanisms for carbon, nitrogen, sulfur and heavy metals under these different landfill environments were investigated. With this goal in mind, four landfill concepts were used. One reactor was operated as aerobic throughout the landfilling period to better understand the effect of aeration on solid waste degradation. The other one was initially operated under aerobic conditions (pretreatment) and then switched to anoxic/anaerobic environment in the second phase (traditional landfilling). Under this scenario, aerobic conditions was investigated for the possible effects on the enhancement of hydrolysis process which ultimately would increase the methane yield. The third reactor was operated under anaerobic conditions in the first phase (traditional landfilling) and then transformed to aerobic environment in the second phase (aerobic remediation). To understand and compare the effect of aeration, the last reactor was operated as an anaerobic bioreactor which represent conventional sanitary landfill conditions. All reactors were operated under wet-tomb management strategy by using leachate recirculation.

The specific objectives of this research are to;

- investigate the behaviour of different landfilling options available for sustainable landfill management
- compare the performance of bioreactor landfills aerobic versus anaerobic

- understand attenuation mechanisms for carbon, nitrogen, sulfur compounds under aerobic and anaerobic conditions
- follow the long-term fate of metals in bioreactors and determine the impacts of changes in redox/pH conditions in the different landfill options.

4. MATERIALS AND METHODS

4.1 Reactor Experiment

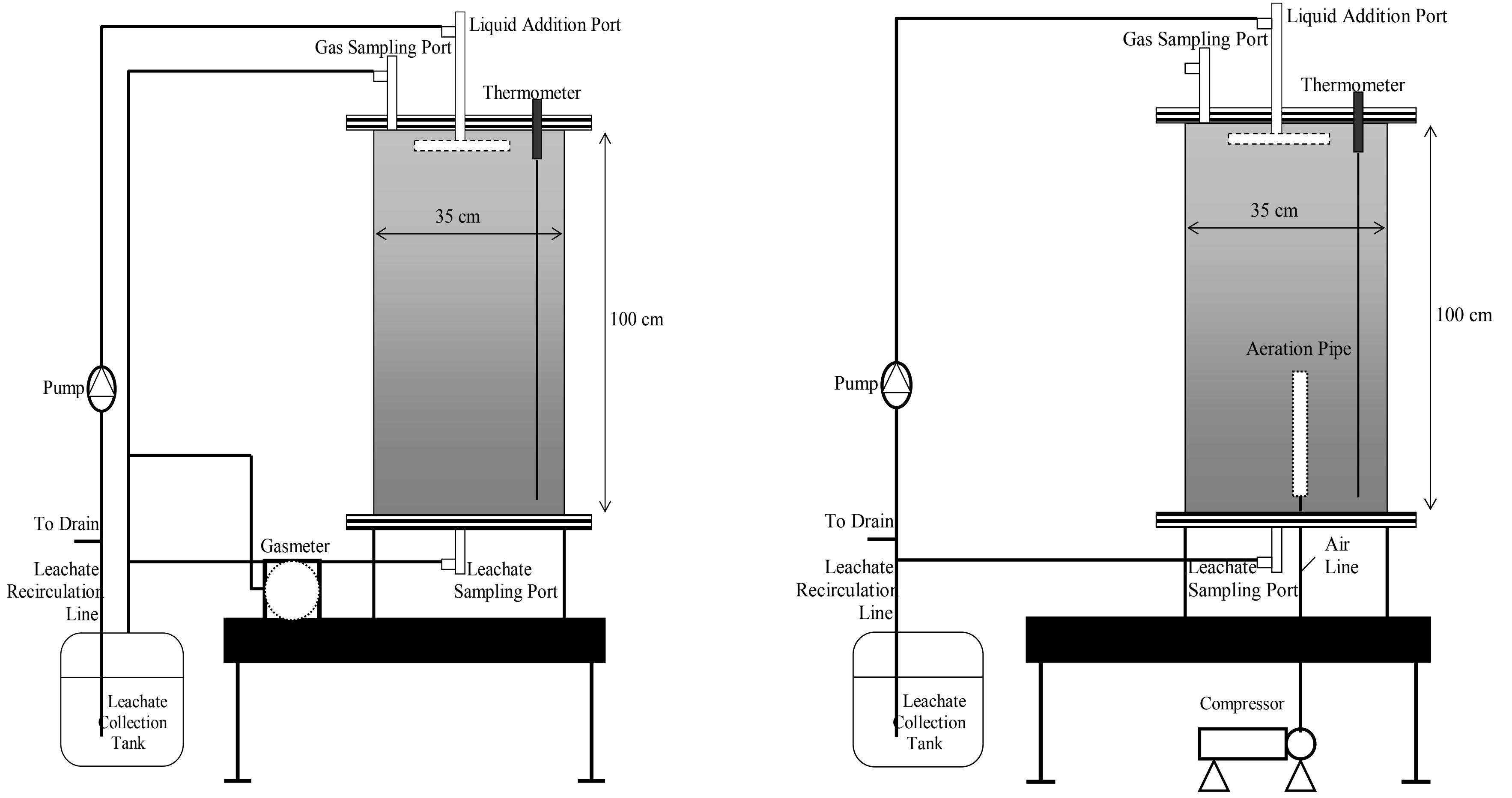
4.1.1 Configuration of the Simulated Landfill Reactors

A schematic of the simulated landfill bioreactors having aerobic and anaerobic digestion processes were constructed in the laboratory are shown in Figure 4.1. A photo display of the experimental set-up is also presented in Figure 4.2.

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.

The reactors were equipped with three ports; one port was used to drain and sampling the leachate while other two ports were used to collect gas samples and to add liquid. 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 and also, attached to other end of the tee, was connected to the leachate plastic container and functioned as a leachate recycle line. A PVC tee was placed in the 1 cm diameter hole. One end of the tee was attached by 0.75 cm Masterflex hose. For anaerobic reactors, the hose was connected to the leachate collection container and functioned as a pressure balance and gas collection line, while the other end of the tee was capped by a rubber septum and functioned as a gas sampling port.



a) Anaerobic b) Aerobic

Figure 4.1. The design and operational features of the simulated landfill bioreactor


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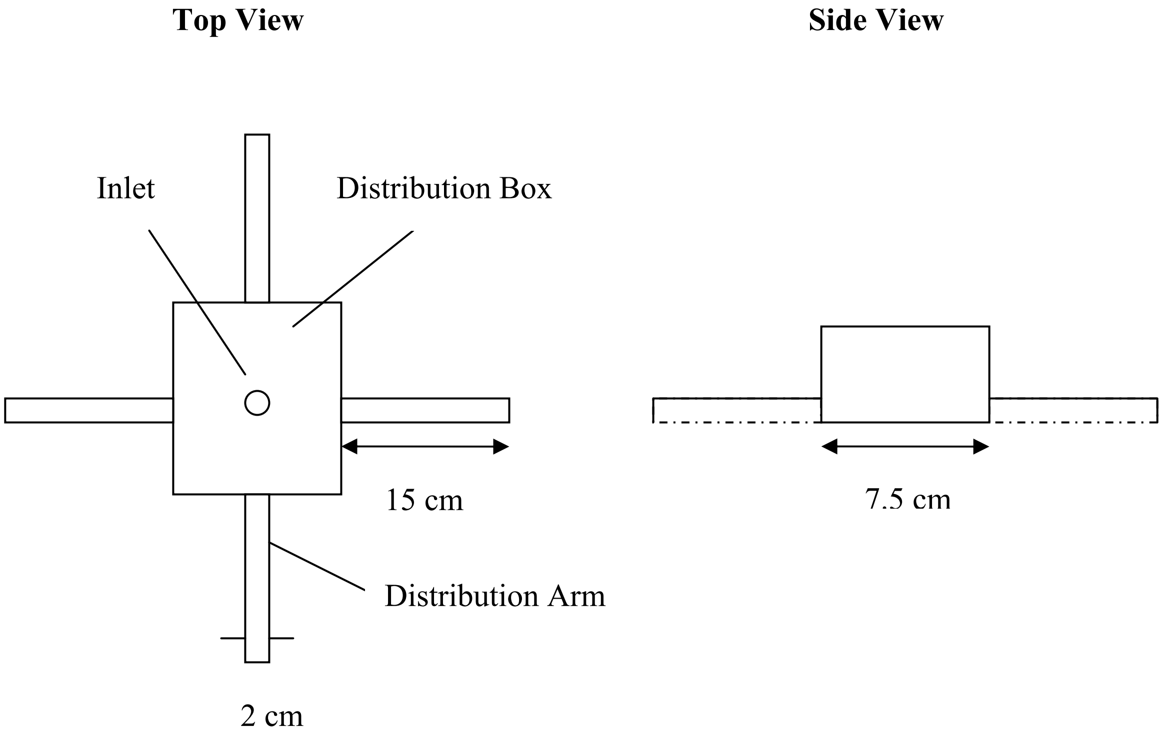
Figure 4.2. Experimental set-up

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 4.3. 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 endcaps 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.


Top View

Side View

(NOT TO SCALE)

Figure 4.3 Leachate distribution system

To determine daily temperature changes in the bioreactors, thermocouples were placed 10 cm radially apart from the liquid addition port at the top lid.

An ISMATEC S460 MINI pump was used to deliver leachate collected in the plastic container to the reactors. 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 reactors.

Air for aerobic reactors was provided by using **Boyu Air Pump S-4000** (Figure 4.4). Air pump was connected to air distribution pipe at the bottom of the reactor. Aeration pipes was made of 2 cm diameter PVC with a lengh of 0.75m. The pipe has 0.5 cm holes drilled with 2 cm spacing (Figure 4.1).

The inside bottom of each reactor was filled by all purpose landscaping gravel to form a leachate drainage zone. The gas produced from reactors (Figure 4.4) was collected and measured using wet gasmeters (Shinagawa Corporation).

Figure 4.4. Air pump and wet gasmeter used for the reactors

Reactors were placed in the 32°C hot room to provide mesophilic conditions for the growth of desired microbial community.

4.1.2 Simulated Landfill Reactors Loading

Simulated landfill reactors were loaded with shredded and compacted solid waste mixture of 19.5 kg. Shredded solid waste in the reactors were prepared synthetically to assure accelerated stabilization, establish the identity and maximize the homogeneity of refuse. The synthetic solid waste mixture represents typical solid waste composition determined for Istanbul region as indicated in Table 4.1.

Table 4.1. Synthetic solid waste composition (www. istac.com.tr)

Composition	Percentage (%)
Organic Material (food + garden)	45
Paper	14.5
Plastic	9.5
Textile	5.6
Glass	3.8
Metal	2.2
Ceramic,	4.4
Other Materials (dust, wood, brick, miscellaneous)	15

The mixtures of approximately 20 kg solid waste were prepared separately for each reactor. Representative samples of 500 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 thick layer of all purpose gravel was placed on the nylon screen. About 19.5 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 233 kg/m^3. 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. Anaerobic reactors were purged with nitrogen gas to displace oxygen from the system and to directly establish the anaerobic conditions.

4.1.3. Simulated Landfill Reactors Operation

In this study, four landfill concepts were used as presented in Table 4.2. From these reactor, one was operated as aerobic throughout the landfilling period to better understand the effect of aeration on solid waste degradation. Aerobic reactor (Reactor 3) was operated for 374 days. Reactor 4 was initially operated under aerobic conditions (pretreatment) and then switched to anoxic/anaerobic environment in the second phase (anaerobic bioreactor landfilling). Under this scenario, aerobic conditions was investigated for the possible effects on the enhancement of hydrolysis process which ultimately would increase the methane yield. The reactor was converted to anaerobic conditions on day 75. Reactor 2 was operated under anaerobic conditions in the first phase (anaerobic bioreactor landfilling) and then transformed to aerobic environment in the second phase (aerobic remediation). The reactor was converted to aerobic conditions on day 264. To understand and compare the effect of aeration, Reactor 1 was operated as anaerobic bioreactor which represents conventional sanitary landfill conditions. This reactor was operated 630 days. All reactors were constructed under the wet-tomb management strategy by using leachate recirculation.

Table 4.2. Operational conditions adopted in the reactors to simulate different landfill concepts.

Reactor	Operating Conditions	Landfill Concept
1	Anaerobic	Anaerobic Bioreactor Landfill
2	Anaerobic/Aerobic	Aerobic Remediated Biorector Landfill
3	Aerobic	Aerobic Bioreactor Landfill
4	Aerobic/Anaerobic	Aerobic Pre-treated Bioreactor Landfill

4.1.3.1 Moisture Application and Management. Simulated landfill reactors received distilled water additions until field capacity was attained and leachate production commenced. As a result, the first phase of landfill stabilization, initial adjustment, was significantly shortened. Preliminary analysis indicated that the solid waste had between 49% and 63% moisture content. To be sure that the moisture content was sufficient for waste to reach field capacity, to commence producing leachate, one liter of water was introduced to each reactor at the beginning of the experiment. The one liter water application procedure was constantly repeated until the amount of liquid introduced was equal to the amount of liquid collected to reassure that field capacity is reached. The total volume of water applied to each reactor until the field capacity was attained, was 6.5 liters for Reactors 1 & 4 and 7 liters for Reactor 2 & 3. This day was defined as Day 0 as presented in the graphics. Fraction of the leachate obtained from each reactor on Day 1 were 2.370 liters from Reactor 1, 2.150 liters from Reactor 2, 2.750 liters from Reactor 3 and 2.300 liters from Reactor 4. Leachate was stored in 18 L plexi-glass bottles for subsequent use and/or analysis.

Throughout the study period, 1 L of collected leachate in storage bottles was recycled to reactors once per week. Moreover, 500 mL/week distilled water, corresponding to an equivalent of 20 cm/year rainfall, was added to the reactors.

4.1.3.2. Temperature Control. The temperature at the center of a full-scale landfill usually remains constant because the garbage and cover soil serve to insulate the system (McBean et al., 1995). In a laboratory environment, however, the heat produced by biologically degrading waste is not sufficient to maintain a temperature close to those normally encountered in a landfill. Therefore, a temperature control room was used to maintain desired temperatures without extreme fluctuations. During the experimental period, the thermo-insulated room was maintained at a constant temperature of 32 ºC for mesophilic waste decomposition.The temperature of each reactor was measured using a type T thermocouple wire (SRT201-160, Omega) fixed on the inside of each reactor (Figure 4.5).

Figure 4.5. Thermocouple and temperature reading

4.1.3.3 Air Injection. The aeration was achieved by an air pump (Model No. 7550-10) that was connected to the aeration pipes at the bottom of each reactor. Air was passed through the waste in an upward direction. In this study, air flow rate was used as 0.11 L/min/kg waste for Reactor 3 & 4. Aeration was applied for 5 hours per day. In Reactor 2, waste is stabilized anaerobically until day 265 and then the reactor is converted to aerobic process. In this reactor, air flow rate (0.11 L/min/kg waste) was applied as 1 minutes per day from day 265 to the end of experiments because it was reported that oxygen requirements ranged from 9 mm^3/g/hr for mature compost to 284 mm^3/g/hr with fresh compost (Diaz, 1998)

4.2 Sampling and Analytical Methods

4.2.1 Sampling

500 g representative solid waste samples has been taken prior to the loading and after disassembling of the reactors. Samples analyzed immediately after dried on oven. Leachate samples of 100- 250 ml were taken from the port at the bottom of the reactors for 3 times in week and analyzed immediately. On the other hand, for trace metal analysis samples were stored at -4 ^{0}C with addition of acid as prohibitive.

4.2.2 Preliminary Analysis of Waste Matrix

Preliminary analyses on the waste mixture provided data required to characterize the landfill materials. Collected solid waste samples were monitored for moisture content, volatile solid, elemental (C,H,O,N,S), density and trace metal (Fe, Mn, Cu, Ni, Cd, Zn, Cr) analysis

4.2.3 Leachate and Gas Analysis

The collected leachate and gas samples were monitored on a regular basis to understand the degree of waste stabilization in the bioreactors. Leachate samples collected from the bottom of the bioreactors were analyzed for chemical oxygen demand (COD), Total organic carbon (TOC), biochemical oxygen demand (BOD), volatile fatty acids (VFA), pH, oxidation-reduction potential (ORP), conductivity, salinity, color, alkalinity, sulfate, sulfide, phosphate, chloride alkali and alkaline earth metals and selected trace metals (Fe, Mn, Cu, Ni, Cd, Zn, Cr). The volume of daily gas production and its composition were monitored throughout the study. All these analyses were performed according to Standard Methods for the Examination of Water and Wastewaters (APHA, AWWA-WEF, 1998).

The gas produced in the reactors was collected and analyzed for quantity and composition. The volume of gas produced was determined daily by wet gasmeters (Shinagawa Corporation). The gas composition in the headspace (O_2, N_2, CO_2 and CH_4) was analyzed using an HP 6850 gas chromatograph (Carboxen 1010 plot column 30 m x 0.53 mm) equipped with a thermal conductivity detector (TCD).

The methods used for the gas and leachate analysis from simulated landfill reactors are summarized in Table 4.3.

Table 4.3. Methods used for leachate and gas analyses of the reactor systems and the frequency of sampling

PARAMETER	FREQUENCY	METHOD	INSTRUMENT
pH	3/week	4500-H B Method Electrometric (APHA, AWWA-WEF-1998)	ORION SA 520 pH meter
ORP	3/week	2580 B Method (APHA, AWWA-WEF-1998)	ORION SA 520 pH meter
Conductivity	1/week	2510 B Method (APHA, AWWA-WEF-1998)	WTW LF 320 Conductivity meter.
Salinity	1/week	2520 B Method (APHA, AWWA-WEF-1998)	WTW LF 320 Conductivity meter.
Color	1/week	2120 C Method (APHA, AWWA-WEF-1998)	HACH DR/3 Spectrophotometer
Turbidity	1/week	2130 B Method (APHA, AWWA-WEF-1998)	HACH 2100P Turbidimeter
COD	2/week	5220 D Method Closed Reflux, Colorimetric (APHA, AWWA-WEF-1998)	HACH COD digester ; HACH DR/3 Spectrophotometer
TOC	1/week	5310 D Method (APHA, AWWA-WEF-1998)	Shimadzu TOC-V CSH Analyzer
BOD_5	1/week	5210 B Method 5-Day BOD Test (APHA, AWWA-WEF-1998)	Dissolved Oxygen Meter HACH model 16046
VFA	1/month	Gas Chromatograph	Gas Chromatograph HP 5890
Acidity	1/week	2310 B Method Titration (APHA, AWWA-WEF-1998)	-
Alkalinity	1/week	2320 B Method Titration (APHA, AWWA-WEF-1998)	-
TKN	1/month	4500 Method (APHA, AWWA-WEF-1998)	HACH Digester
Ammonia-N	1/week	4500 E Method Titration (APHA, AWWA-WEF-1998)	Gerhardt Vapodest Disstillation Apparatus

Total P	1/month	4500-P E Method Ascorbic Acid (APHA, AWWA-WEF-1998)	HACH Digester
Orthophosphate	1/week	4500-P E Method Ascorbic Acid (APHA, AWWA-WEF-1998)	HACH DR/3 Spectrophotometer
TS, TSS, TDS	1/month	2540 Method (APHA, AWWA-WEF-1998)	-
Chloride	1/month	4500-Cl B Method Argentometric (APHA, AWWA-WEF-1998)	-
Sulfate	1/week	4500-SO_4^{-2} E Method Turbidimetric (APHA, AWWA-WEF-1998)	HACH DR/3 Spectrophotometer
Sulfide	1/week	4500-S^{-2} E Method Iodometric (APHA, AWWA-WEF-1998)	-
Heavy Metals	1/month	ASTM 3010	Perkin Elmer Inductively Coupled Plasma (ICP-OES)
Gas Production	Daily	Wet Gasmeter	Gasmeter
CH_4, CO_2, O_2, N_2	1/week	Gas Chromatograph	Gas Chromatograph HP 6850

4.2.4 Bioreactor Disassembly and Final Analyses

Upon completion of the study, bioreactors were disassembled. Leachate produced by each reactor was allowed to drained prior to the disassembly. Waste samples were collected and prepared representative samples to analyze for moisture, volatile solids, metals and C/N/H/S/O content. Results from the preliminary analysis of waste were compared to the results from the final analysis. Additionally, a visual inspection of the waste was conducted to based on the apperance of the samples taken from each reactors.

5. RESULTS AND DISCUSSION

During the experimental period, solid waste, leachate and gas produced from the bioreactors were analyzed for the parameters indicative of landfill stabilization as well as for the behavior and fate of the organic and inorganic pollutants under aerobic and anaerobic conditions. These parameters provide the basis for determining efficacy and guidance on optimum operational conditions for process control.

5.1. Preliminary Solid Waste Analysis

Preliminary analyses on the waste mixture provided data required to characterize the landfill materials. The determination of initial moisture content in the waste was important information for establishing moisture required to reach field capacity and leachate requirements for the operation of the reactors. The ultimate analysis involving the determination of the percent C(carbon), H(hydrogen), O(oxygen), N(nitrogen), S(sulphur) and ash were used to characterize organic composition in the waste mixture. It was also used to define the mix of waste materials and to ensure nutrient availability for biological conversion. The initial characteristic of the waste was determined using the analytical techniques described in Section 4.2, the results of which are summarized in Table 5.1.

The heavy metal analyses of the solid waste samples were also performed in order to detect possible heavy metal inhibition in the systems and are given in Table 5.2. Heavy metals can be inhibitory to microbial life above threshold concentrations even though trace amount of metals are necessary for microorganisms. The major sources of heavy metals in landfills come from household hazardous substances such as batteries, paints, dyes, inks in paper (Förstner et al., 1991). The most common heavy metals disposed to landfills are iron, manganese, zinc, nickel and copper.

Table 5.1. Characteristics of waste used as the waste matrix in the landfill bioreactors

Component	**Reactor 1**	**Reactor 2**	**Reactor 3**	**Reactor 4**
Initial Wet Weight (kg)	19.50	19.50	19.50	19.50
Initial Dry Weight (kg)	9.56	9.95	7.22	7.22
Wet Density (kg/m^3)	236	231	236	228
Carbon (%)	43.09	42.62	45.41	48.46
Nitrogen (%)	1.49	1.63	1.47	1.52
Hydrogen (%)	6.74	6.78	7.43	6.87
Oxygen (%)	35.95	33.55	33.34	32.01
Sulfur (%)	-	-	-	-
C/N	28.92	26.15	30.89	31.88
Volatile Solids (%)	82	86	84	84
Moisture Content (%)	51	49	63	63

Table 5.2. Heavy metal concentrations in solid waste samples

	Reactor 1	**Reactor 2**	**Reactor 3**	**Reactor 4**
Fe (mg/kg)	1705	1727	1482	2223
Mn (mg/kg)	83	89	61	80
Ni (mg/kg)	15	14	10	9
Zn (mg/kg)	48	59	44	58
Cd (mg/kg)	1.6	0.9	0.9	0.9
Cu (mg/kg)	27	15	15	33
Cr (mg/kg)	0,2	0	0	0,7
Pb (mg/kg)	30	38	23	33

5.2. Water Balance

Preliminary analysis indicated that the solid waste contained between 49% and 63% moisture. From the moisture analysis of the solid waste, initial water was determined to be 9.94 L for Reactor 1, 9.55 L for Reactor 2, 12.28 L for Reactors 3 & 4. Simulated landfill reactors received distilled water additions until the field capacity was attained and leachate production commenced. The total volume of water applied to each reactor was 6.5 liters for Reactors 1 & 4 and 7 liters for Reactors 2 & 3. This was set as Day 0.

Throughout the study, 500 mL/week distilled water, corresponding to an equivalent of 20 cm/year rainfall, was added to each reactors. Totals of 37 L, 37.5 L, 24 L and 23.5 L of distilled water were added to Reactors 1,2,3 and 4, respectively (Figure 5.1). Moreover, 1 L of leachate collected in leachate tanks was recycled to reactors once per week. Total of 74 L, 72 L, 46 L and 47 L of leachate was recycled to Reactors 1,2,3 and 4, respectively (Figure 5.1). More water added and recycled to Reactors 1 and 2 because these reactors have more operation days.

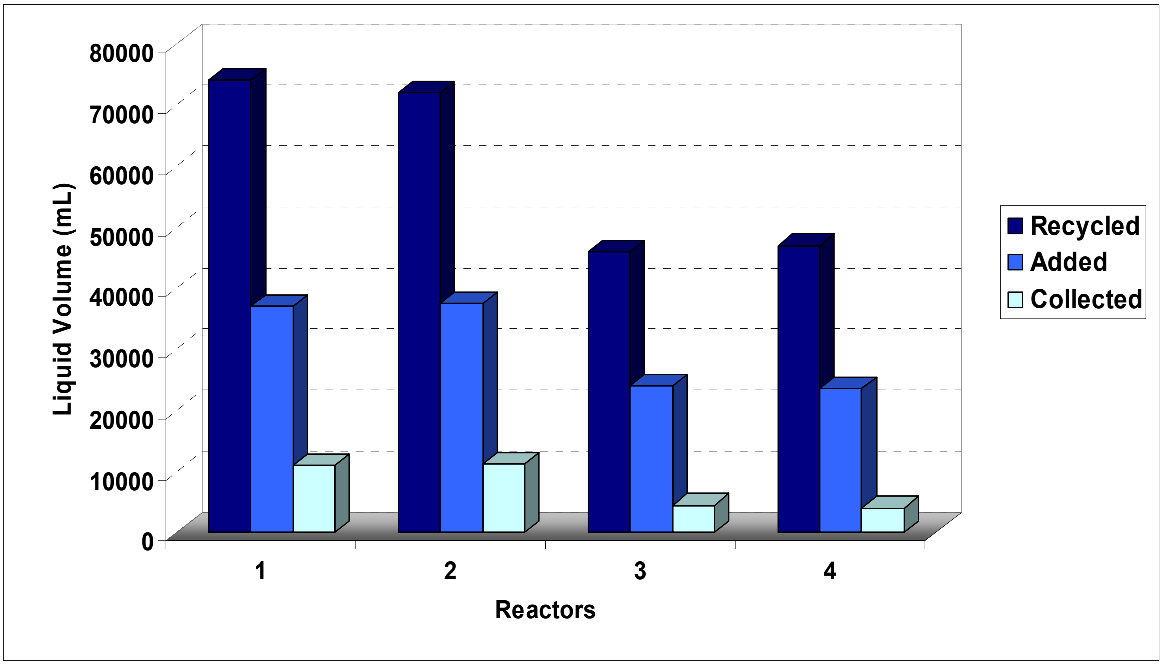


Figure 5.1. Total volume of liquid recycled, added and collected in the reactors

Leachate from the reactors was removed for sampling purposes only. Leachate was also removed from each reactor as a result of moisture losses during gas production.

Therefore, the amount of moisture lost due to gas production was calculated for each reactor based on the following assumptions: (i) the total system pressure is equal to 1 atmosphere, (ii) the volume of gas collected is saturated with moisture, and (iii) the density of water is 1000 g/L. The volume of water lost due to the gas production was calculated as follows:

$$V_{LOST}=\frac{q*\rho_{GAS}}{MW_{H_2O}*55.6\ Moles/L} \qquad (5.1)$$

where;
V_{LOST}= Volume of water 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_{H2O}=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:

$$q=\frac{0.622*(VP)}{P_T-[0.378*(VP)]} \qquad (5.2)$$

where;
VP=Water vapor pressure at specified temperature (kN/m^2),
P_T=Total system pressure (101.325 kN/m^2)

At 32°C water vapor pressure is estimated to be 4.75 kN/m^2 (http://en.wikipedia.org/wiki/Vapor_Pressure_of_Water_at_Various_Temperatures). When substituted in equation (5.2) specific humidity is calculated to be 0.0297 g H_2O/ g gas.

The gas density can be calculated using the ideal gas law, provided that the molecular weight of the gas is known. Molecular weight of gas was determined using the following equation:

$$MW_{GAS}=MW_{CO2}*X_{CO2}+MW_{O2}*X_{O2}+MW_{N2}*X_{N2}+MW_{CH4}*X_{CH4} \qquad (5.3)$$

where;

MW_{GAS}= Molecular weight of gas mixture (g/mole)
MW_i=Molecular weight of each component gas (g/mole)
MW_{CO2}=44.010 g/mole
MW_{O2}=31.999 g/mole
MW_{N2}=28.013 g/mole
MW_{CH4}=16.043 g/mole
X_i=Mole fraction of gas_i (moles gas_i/total moles gas)

Using Henry's law mole fraction of carbon dioxide, nitrogen, oxygen and methane at 32 °C were calculated. Substituting the values in the equation (5.3) molecular gas mixture weight of each reactor is calculated to be 6.4×10^{-3} g/mole for Reactor 1, 4.9×10^{-3} g/mole for Reactor 2, 1.5×10^{-3} g/mole for Reactor 3, 5.2×10^{-3} g/mole for Reactor 4. Therefore, gas density is calculated to be:

$$\rho_{GAS} = \frac{MW_{GAS} * P_T}{R * T} \qquad (5.4)$$

where;
R=Universal gas constant (0.0821 L*atm/K*mole]
T=Temperature [K] = 273 + 32 = 305 K

Thus, by combining Equations (5.3) and (5.4) and substituting along with Equation (5.2) into Equation (5.1), the volume of water removed by the gas produced was determined. Results of these calculations are presented in Table 5.3.

Table 5.3. Water removed due to gas production

Reactors	Reactor 1	Reactor 2	Reactor 3	Reactor 4
V_{LOST} (L H_2O/L gas)	7.5×10^{-9}	5.7×10^{-9}	7.5×10^{-9}	7.5×10^{-9}

Knowing that Reactor 1 produced 1497 L of gas, volume of liquid lost due to gas production in Reactor 1 was determined to be 1.12×10^{-5} L. The same procedure could not be used for determination of water lost for the reactors operated under aerobic conditions since gas production could not measured from these reactors. However, it was assumed that cumulative volume of water removed by gas production from these reactors to be insignificant in comparison with the volume of water removed for sampling.

Final waste analysis indicated that the solid waste had moisture content between 64 % and 68 %. From the moisture analysis of the solid waste, water content was determined to be 10.07 L for Reactor 1, 10.09 L for Reactor 2, 10.12 L for Reactor 3 and 11.19 L for Reactor 4.

The volume of water retained in each reactor in excess of the field capacity was also calculated. Parameters used in water balance included: (i) volume of recirculated leachate; (ii) supplemental liquid addition; and (iii) measured leachate generation and sampling. It is also important to take into account (iv) the moisture content of the incoming and outgoing waste. Moisture generated as a result of biological or chemical interactions within the landfill cells was neglected as a source of additional liquids in the moisture balance calculations. Moisture leaving the landfill through the gas collection system as condensate was also not included in the moisture balance calculations. These two sources were not expected to significantly influence the results of the analysis expressed as percentage.

The amount of water retained in each reactor was calculated as follows:

$$W_{in}-W_{out} \pm W_{reaction} = \Delta W \qquad (5.5)$$

where;

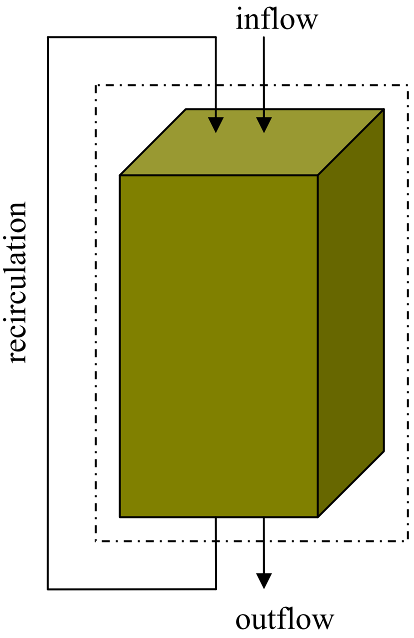
ΔW = net water storage in the reactors

W_{in} = initial waste moisture content + recirculation + water addition

W_{out} = final waste moisture content + recirculation + sampling + collection

$W_{reaction}$ = 0 (assumption)

Using the water balance approach;



Reactor 1

(9.94+74+37)-(10.07+74+24+11)=1.87 L

Reactor 2

(9.55+72+37.5)-(10.09+72+23.55+11.25)=1.35 L

Reactor 3

(12.28+46+24)-(10.12+46+13.6+4.5)=8.06 L

Reactor 4

(12.28+47+23.5)-(11.19+47+13.6+4)=6.99 L

After 374 days of operation, Reactors 3 and 4 were found to hold a total of about 8.06 and 6.99 liters while Reactors 1 and 2 operated under anaerobic conditions held 1.87 and 1.35 liters of water on Day 630, respectively. As a result, leachate treatment needs of aerobic landfill reactor were reduced by over 30%. It is estimated that this reduction of effluent leachate volume in aerobic reactors is caused, in part, by the evaporative effects of the higher reactor temperatures and the effects of air-drying out the waste. Studies associated to this effect are ongoing, including evaluations of waste mass field capacity (Read et al., 2001a). Hudgins and Green (1999) estimated a decrease in leachate volume from aerobic cells of about 86% at Columbia Country Landfill and 50% at Live Oak Landfills.

5.3. Leachate Analysis

5.3.1. pH

Leachate pH values of reactors were monitored routinely throughout the experimental study due to their importance as indicator parameter in waste stabilization. The pH of system depends upon the relationship between the volatile acid concentration and alkalinity in the leachate and carbon dioxide content in the gas phase produced during the stabilization process. In general under anaerobic conditions, acid forming bacteria have an optimum pH range of 5.0-6.0. On the other hand, methane formation will proceed in pH range of 6.5-8.0. The optimum pH for methane generation is given as 7.0-7.2 (Emcon Associates, 1980).

The change in leachate pH from the reactors is given in Figure 5.2. Initial pH values of the Reactors were 5.83 for Reactor 1, 5.40 for Reactor 2, 5.83 for Reactor 3 and 5.31 for Reactor 4, respectively. All reactors were acidic at the beginning of the experiment. However, low pH in aerobic reactors (Reactor 3 and 4) became neutral in few days and was measured between 7.5 and 8.0 after day 35 until the end. The conversion of the Reactor 4 from aerobic to anaerobic conditions on Day 75 did not affect pH values in the system. pH values stayed at 7.5 enhancing methanogenic growth. Gas production and its CH_4 content of Reactor 4 confirmed the methanogenic conditions. Two stages (acidic and methanogenic or alkaline) of pH in the anaerobic reactors were observed during the experimental period. Initial low pH values in the anaerobic bioreactors (Reactors 1 and 2) increased sharply and reached to 7.0 on Day 446 (Reactor 1) and on Day 146 (Reactor 2) after the onset of methanogenic conditions and then fluctuated between 7.0 and 7.5 until the end of the experiments. In Reactor 1, pH stayed at acidic values for long time due to the accumulation of organic acids. During the acidogenesis phase, excessive production of volatile fatty acids and their accumulation cause retardation of methane generation phase. Barlaz et al (1990) confirmed that acids accumulate and pH decreases due to an imbalance between fermentative and methanogenic activity. On the other hand, in Reactor 2, it was not observed any retardation and pH value did not change after the conversion of the reactor from anaerobic to aerobic conditions and was between 7.2 and 8.0.

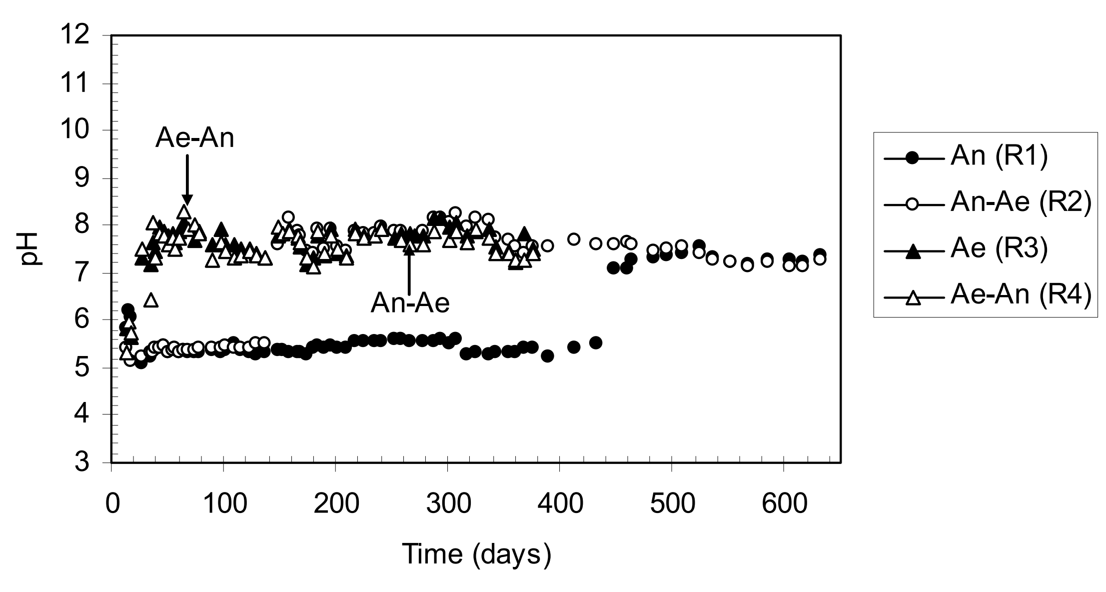


Figure 5.2. Leachate pH values

As can be seen from the Figure 5.2, the pH of aerobic reactor was more alkaline than the pH from anaerobic reactor due to CO_2 stripping air flow; a decrease in CO_2 leads to a decrease in carbonic acid (H_2CO_3) and bicarbonate ion concentrations (HCO_3^-) consuming H^+ ions (Kim, 2005). This observation was also confirmed by Stessel and Murphy, 1992; O'Keefe and Chynoweth, 2000; Agdag and Sponza, 2004; Kim, 2005 in literature. The range of pH of aerobic reactors has been reported as 7.0-9.0.

5.3.2. ORP

ORP is a physical-chemical parameter that indicates the oxidation-reduction potential of the system. The ORP is particularly important in defining the chemical characteristics of the landfill environment. The chemical environment of a sanitary landfill is typically reducing due to biologically mediated oxidation-reduction reactions. Measured ORP values for reactors are presented in Figure 5.3.

ORP values in all reactors exhibited similar behavior ranging between −328 and 0 mV during the first 75 days (Fig. 5.3). Aerated reactors had more negative values than anaerobic reactors due to rapid organic degradation. Low ORP values of leachate for aerobic reactors were caused by leachate accumulation in the reactors. Since injected air can travel in the unsaturated upper zone only, leachate accumulated at the bottom remained anaerobic. This was also confirmed by black color and hydrogen sulfide smell of the samples. After Day 75, the ORP values for aerobic reactors increased slightly and positive values were observed as the study progressed and reached to about +150 mV. The results of ORP in the aerobic reactor are similar to the findings of Inanç et al. (2007), who reported ORP values in aerobic cells exhibited similar behavior and ranged between −350 and −500mV during first 200 days. On Day 226, all leachate was pumped out after sampling. As a result, ORP has jumped to +85mV on the next sampling (Day 239).

Oppositely, ORP values decreased below -200 mV in Reactor 2 after 140 days, which showed that the degradation was changing from the acidogenic phase to the methanogenic phase after the consumption of the available oxygen in the anaerobic reactor. Some researchers found that there is an optimum ORP requirement for methanogenesis, which generally ranges from -100 to -300 mV (Pohland et al., 1993). After addition of air into Reactor 2, ORP values, firstly decreased to lower values due to ongoing organic degradation of waste and accumulation of it in leachate and then increased to positive values at the end of study. In Reactor 1, ORP values decreased to more negative values together with the onset of methanogenic conditions after Day 430 and changed between -80 and -379 mV.

Moreover, a negative oxidation–reduction potential (ORP) is indicative of microbially mediated reduction of sulfate to sulfide and nitrate to ammonium. Since sulfides form very sparingly soluble precipitates with many heavy metals, and ORP levels become even more negative during methane fermentation, removal of heavy metals by sulfide precipitation decreases both sulfate pool and leachate heavy metals concentrations (Lee, 1989).

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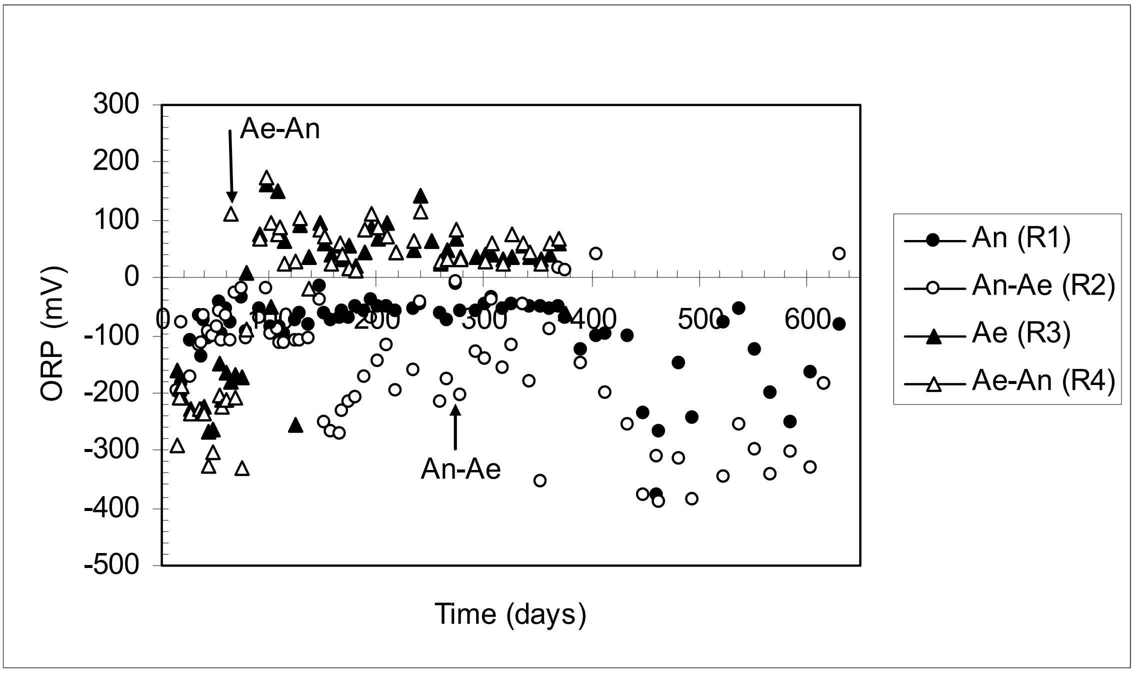

Figure 5.3. Leachate ORP values

5.3.3. Conductivity

The conductivity of a leachate reflects the total concentration of ionic solutes and is a measure of the ability to convey an electric current. This ability depends on the presence of ions, their total concentrations, mobility, valence, relative concentrations and on the temperature of measurement. Solution of most inorganic acids, bases, salts and heavy metals are relatively good conductors. Conversely, molecules of organic compounds that do not dissociate in aqueous solution conduct a current very poorly. In leachate from a young landfill both inorganic and organic species such as free volatile acids contribute to the conductivity. In older leachate, the conductivity is mainly attributed to heavy metals, sodium, potassium and bicarbonate ions and to a lower extent to fulvic acids (Esteves, 1981). The conductivity of the leachate samples collected from the reactors are shown in Figure 5.4.

Initial values of 23.7, 22.6, 16.71 and 16.8 mS/cm for Reactors 1,2,3 and 4, respectively were followed by steady decrease to minimum values 61%, 77%, 50% and 50% of the initial values at the end of study. The decrease in conductivity was due to the washout of easily mobilized ions such as metals, chloride and sulfate combined with such factors as the conversion of sulfate to sulfide under increasingly reducing conditions. The subsequent precipitation of sulfide as heavy metal sulfides would tend to withdraw significant ionic strength from solution.

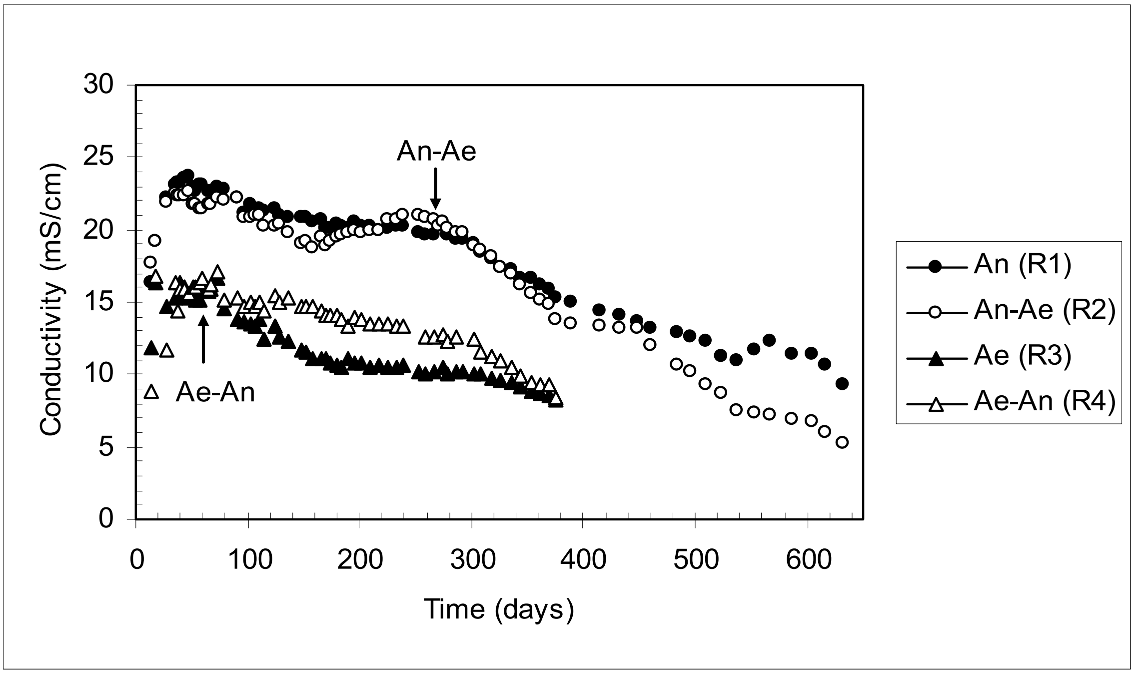

Figure 5.4. Leachate conductivity values

To the extent that they represent relationships among reactants in media at infinite dilution, classical equilibrium constants actually will be in error with respect to conditions present in real aqueous systems. This error will be sufficiently slight and may be neglected in most fresh waters and many wastewaters. However, in systems containing high concentrations of dissolved solids, corrections due to ionic strength cannot be neglected (Pohland et al, 1987). An examination of composition of leachate as determined both in numerous prior studies and in the present work indicates that activity corrections arising from the high ionic strengths in the leachates may be sustantial. Since activity is a function of ionic strength, computation of activity coefficients depends on a knowledge of the ionic strength of the medium involved. Conductivity decreases as the ionic strenght decreases. In this study, ionic strength was estimated on the basis of the empirical linear approximation.

M= Ionic Strength = $1.6\text{x}10^{-5}$ x Conductivity in μmho (Snoeyink and Jenkins, 1980) (5.6)

The values of the ionic strength as a function of time are presented in Figure 5.5. The activity coefficient for reactive species increases as ionic strenght decreases, resulting in greater solubility of ions in solutions such as leachate than in more dilute systems. Activity coefficients were computed for mono-, di- and trivalent ions are presented in Figure 5.6. The activity coefficients indicated in this figure were calculated by means of the extended DeBye-Hückel expression (Snoeyink and Jenkins, 1980 and Pohland et al, 1987).

- For ionic strength of more than approximately 0.1

$$-\log \gamma = \frac{0.5 x Z^2 x\ \mu^{1/2}}{1+\mu^{1/2}} - 0.2\ \mu \qquad (5.7)$$

- For ionic strength of more less approximately 0.1

$$-\log \gamma = \frac{0.5 x Z^2 x\ \mu^{1/2}}{1+\mu^{1/2}} \qquad (5.8)$$

Where; Z is the charge on the ion being considered, μ is the ionic strength, and γ is the activity coefficient.

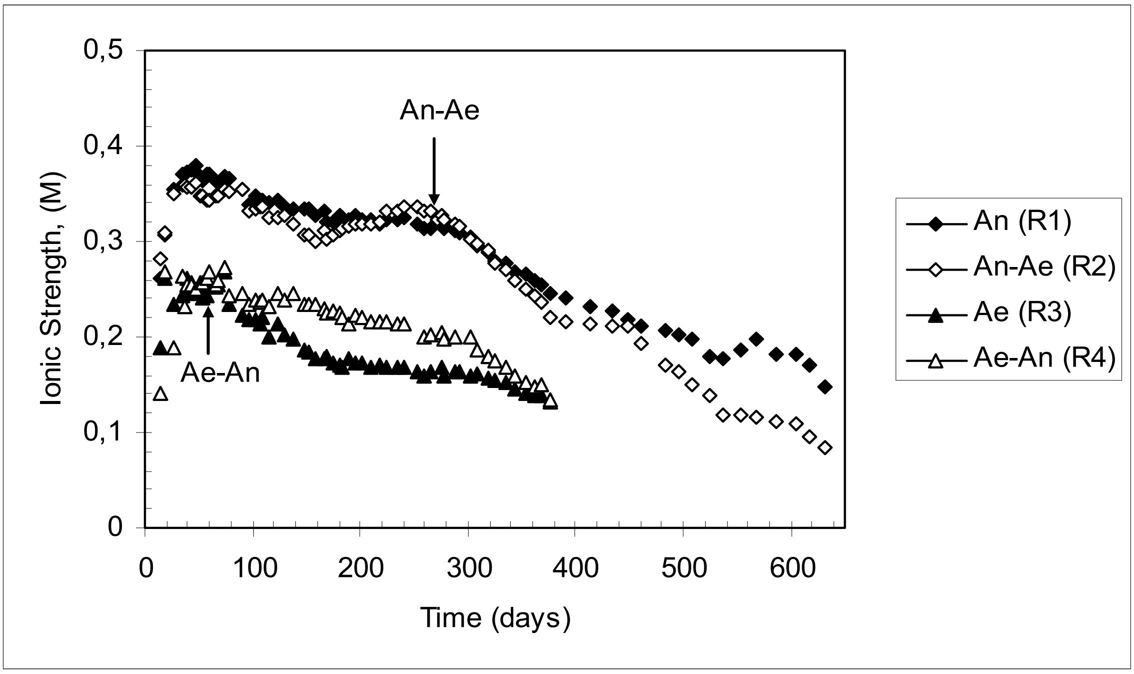

Figure 5.5. Leachate ionic strength values

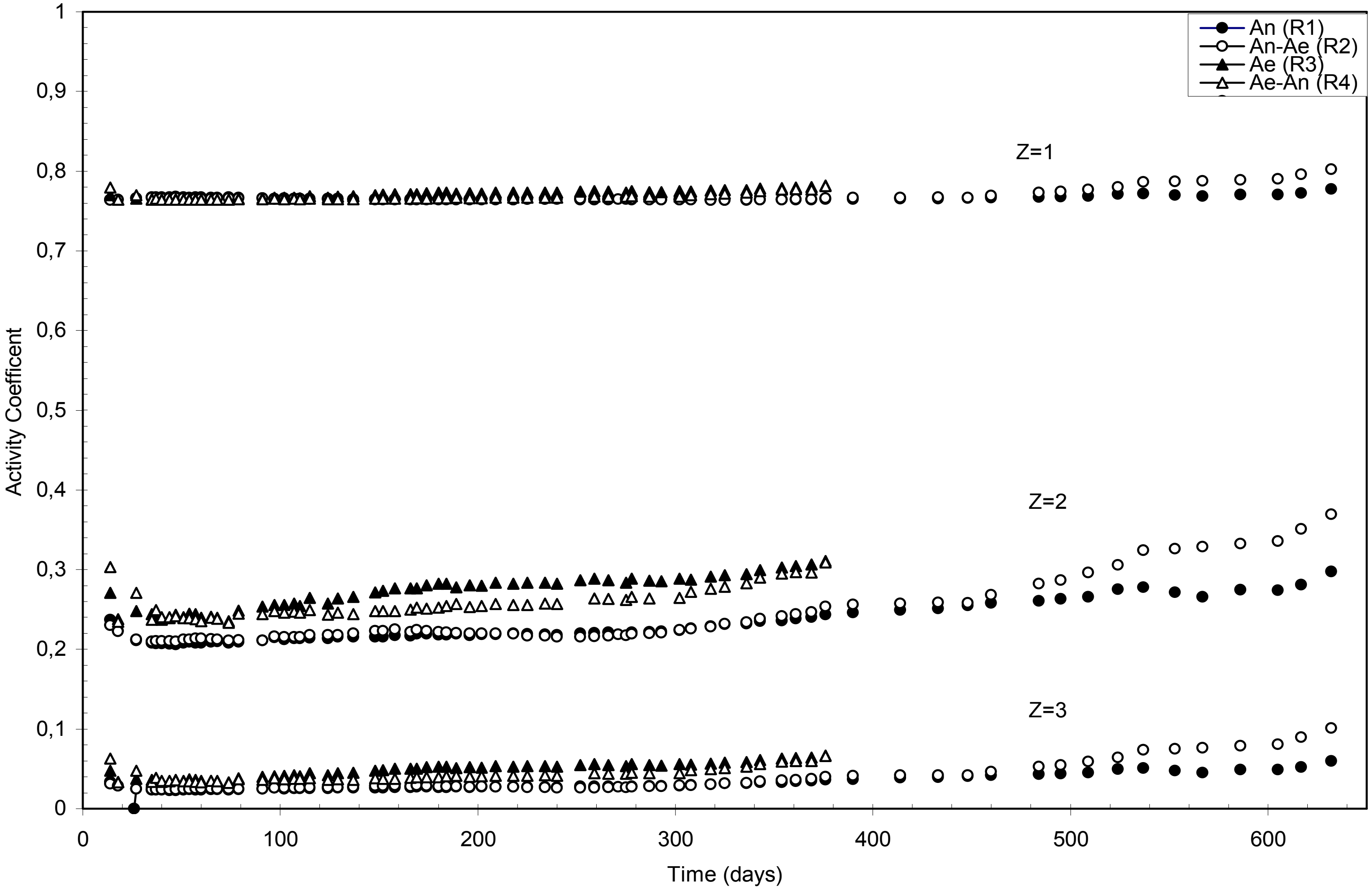

Figure 5.6. Activity coefficients as a function of time

For monovalent ions such as Na^+, K^+, Cl^- the value of γ averaged 0.77 units for all reactor. Divalent ions such as Ca^{+2}, Ni^{+2}, Cd^{+2}, Zn^{+2} and SO_4^{-2} had γ values which averaged 0.23, 0.24, 0.27, 0.26 units for the Reactor 1,2,3 and 4,respectively. Trivalent ions such as Fe^{+3}, PO_4^{-3} were unlikely to be present at any significant levels in these leachates had a γ value of 0.031, 0.036, 0.048 and 0.042 units, respectively. While the high ionic strength characteristic of landfill leachates tended to impose moderate to large activity corrections of individual ionic species, the net impact would generally be so obscured due to the chemical complexity of the landfill environment.

5.3.4. Salinity

Salinity is defined as the total solids in water after all carbonates have been converted to oxides, all bromide and iodide have been replaced by chloride and all organic matter has been oxidized. It was conceived as a measure of the mass of dissolved salts in a given mass of solution. The salinity values from the reactors are shown in Figure 5.7.

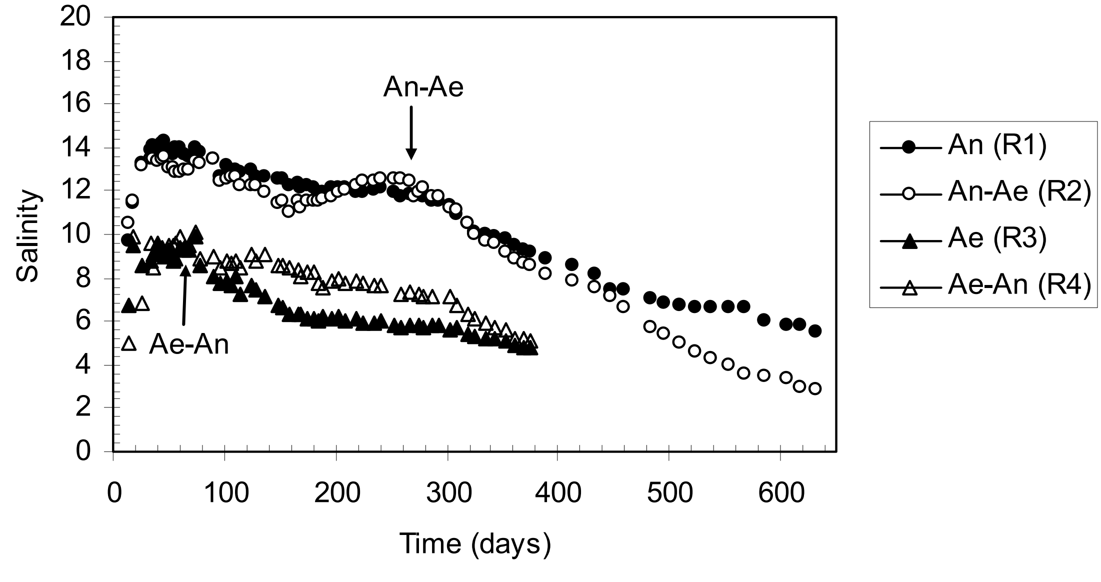

Figure 5.7. Leachate salinity values

Salinity and conductivity showed same decreasing trend in all reactors. Salinity is an unitless parameter. Salinity values first increased to 14.0 in the Reactors 1 and 2 and then decreased to 5.50 in Reactor 1 and 2.90 in Reactor 2 at the end of study (Day 630). On the other hand, salinity values of Reactors 3 and 4 were lower than the values of Reactors 1 and 2 and also continued to decrease to about 5.0 in both reactors. Salinity, total dissolved solids and conductivity correlated linearly with chloride concentration in the reactors. Moreover, the parameters confirmed decrease in salinity trend as a funtion of time because of washout and immobilazation of ions in the reactors.

5.3.5. Color

Color is a noticeable physical characteristic of leachate from the solid waste. Color generally results from organic waste during decomposition. Tannins, humic acid and humates from the decomposition of lignin are considered to be the principal color bodies. Iron is sometimes present as ferric humate and produces a color. The leachate color changed from turbid black to clear yellow and it was attributed mainly to the oxidation of ferrous ions to ferric form and the formation of ferric hydroxide colloids and complexes with fulvic-humic substances (Chu et al., 1994). The black leachate likely resulted from insoluble black sulfide precipitates. Leachate color values from the reactors are presented in Figure 5.8.

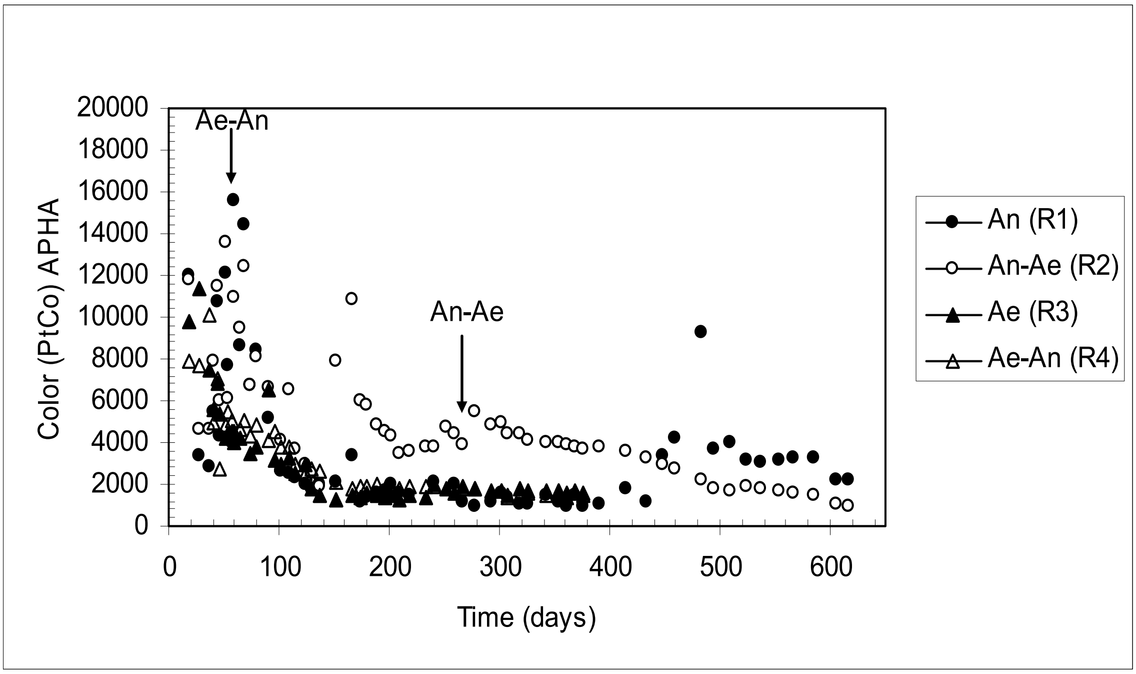

Figure 5.8. Leachate color values

Initial color values were high and they were 12025 PtCo for Reactor 1, 11775 PtCo for Reactor 2, 9825 PtCo for Reactor 3, 7850 PtCo for Reactor 4. As expected, organic degradation plays an important role in leachate color values. Color in Reactors 3 and 4 began to decline rapidly beacuse organic degradation was nearly completed as a result of aerobic conditions. In Reactors 1 and 2, leachate color reached to their higher values in the different times due to rapid conversion of organic acids to methane. Color was 10800 PtCo for the Reactor 2 on Day 164 and 9300 PtCo for Reactor 1 on Day 482. At the end of study color removals of Reactor 1,2,3 and 4 were 86 %, 93 %, 86 %, 85 %, respectively. The highest removal was observed in Reactor 2 converted from anaerobic to aerobic conditions.

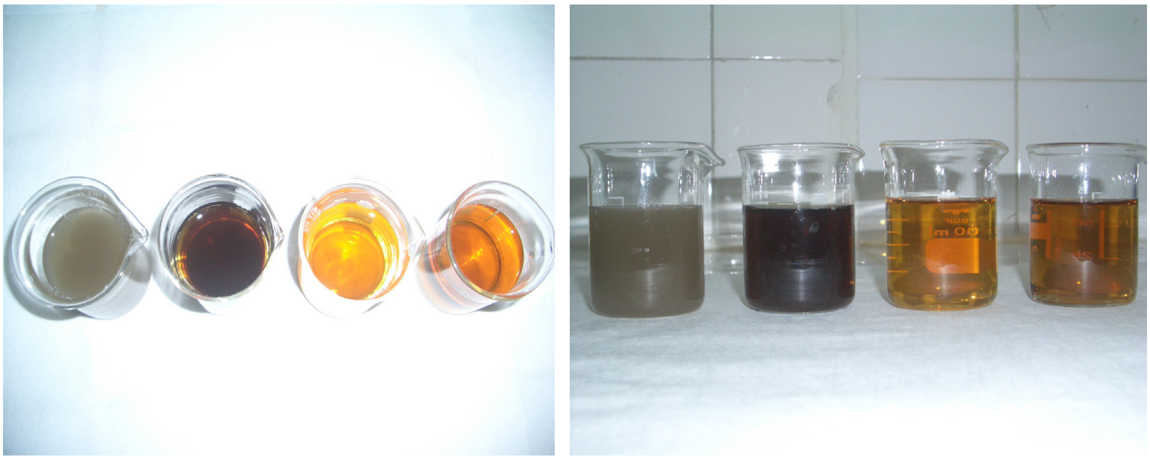

Figure 5.9. Leachate ocular colors in the reactors as a function of time

Figure 5.9 indicates ocular color in Reactors 1,2,3 and 4 at the end of reseach. The color of leachate changed sequentially from gray to dark gray and then to black indicating septic conditions. In most cases, the gray, dark gray and black color of leachate is due to the formation of metallic sulfides, which form as the sulfide produced under anaerobic conditions react with the metals in the leachate. Towards the end of study leachate color changed brown and light brownish color and due to humic substances. To sum up, malodorous black leachate became an inodorous and pale yellow effluent at the end of study.

5.3.6. Turbidity

Turbidity, a measure of the light-transmitting properties of water, was used to indicate the quality of leachate with respect to colloidal and residual suspended matter. Turbidity was measured in units called nephelometric turbidity units (NTUs). Turbidity is caused by the presence of suspended and dissolved matter, such as clay, silt, finely divided organic matter, plankton and other microscopic organisms, organic acids, and dyes. Figure 5.10 shows declining turbidity profiles of the reactors as a function of time.

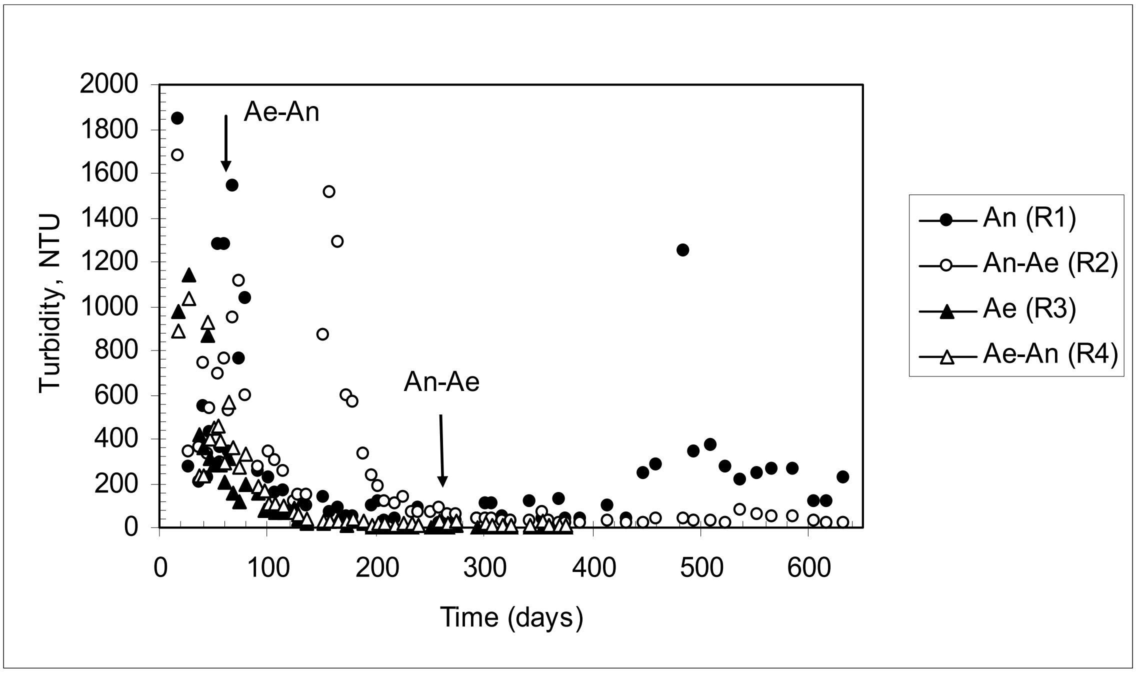

Figure 5.10. Leachate turbidity values

Turbidity and color have similar behavior. Initally, turbidity values were high for all reactors due to colloidal transmission from waste to leachate by water addition in the reactors and rapid degradation of organics in Reactors 3 and 4 that were operated aerobically at the beginning. Until Day 135, turbidity decreased from 1842 NTU to 94 NTU in Reactor 1, from 1678 NTU to 142 NTU in Reactor 2, from 1146 NTU to 22 NTU in Reactor 3 and from 1032 NTU to 37 NTU in Reactor 4. After this day, turbidity values did not exceed 40 NTU in Reactors 3 and 4 and were observed as 2.3 NTU in Reactor 3 and 9.7 NTU in Reactor 4 on Day 374. On the other hand, high turbidity observed in

Reactors 2 and 1 during the experiment because of hydrolysis and anaerobic decomposition of organics. COD, gas production and color parameters confirmed the degradation in the reactors. Turbidity was 1510 NTU for Reactor 2 on Day 156 and 1250 NTU for Reactor 1 on Day 482. Turbidity at the end of study decreased to 120 NTU in Reactor 1 and 20 NTU in Reactor 2.

5.3.7. Chemical Oxygen Demand (COD)

Aerobic or anaerobic conversion process of organic material occurring in a landfill area is the same as that occurring in wastewater treatment systems, with the exception that the effective retention time in a landfill is of the order of years compared to days for wastewater treatment processes. Leachate chemical oxygen demand (COD) is produced in landfills as a result of waste degradation and can provide evidence regarding the progression or inhibition of landfill stabilization processes. Leachate COD concentrations for the reactors are shown in Figure 5.11.

The initial leachate COD concentrations of Reactors 1,2,3 and 4 were 38,022, 36,088, 17,932 and 12,608 mg/L, respectively. COD concentration in the anaerobic reactor (Reactor 1) increased from 38,022 mg/L to 61,973 mg/L due to rapid release and hydrolysis of complex organics from solid waste to the leachate and then remained at the same high concentrations due to the accumulation of organic acids until day 290. This was confirmed with slight decrease in pH values and increase in VFA concentrations during these days. After the onset of methanogenic conditions that was confirmed by gas composition, COD concentrations began to decrease slowly to 30,400 mg/L until day 433 and then declined rapidly to below 900 mg/L at the end of experiment because increased alkalinity in the system prevented the accumulation of volatile organic acids and decreased their undesired effects on methanogens.

The COD values in Reactor 2 (anaerobic to aerobic) rose from 36,088 mg/L to about 55,550 mg/L during anaerobic degradation process. Leachate recirculation accelerated the initiation of organic material conversion which was confirmed by accelerated gas generation rate, increased pH and alkalinity values. A sharp decrease in COD was observed after Day 135. COD values in Reactor 2 began to decrease rapidly from about 44,250 mg/L on Day 135 to 1,796 mg/L on Day 187. After this day, COD concentrations stayed stable until air addition on Day 264. Together with air addition, COD concentrations indicated a slight decreasing trend and dropped to almost 446 mg/L from 1807 mg/L at the end of experiment. Most of the readily biodegradable organics were stabilized during anaerobic degradation process and then aeration helped to nearly complete the conversion of waste.

The COD concentrations in aerobic reactor (Reactor 3) increased to 19,237 mg/L and decreased rapidly after pH was neutralized. The COD concentrations on Days 77 and 374 were determined as 1,596 and 678 mg/L, respectively.

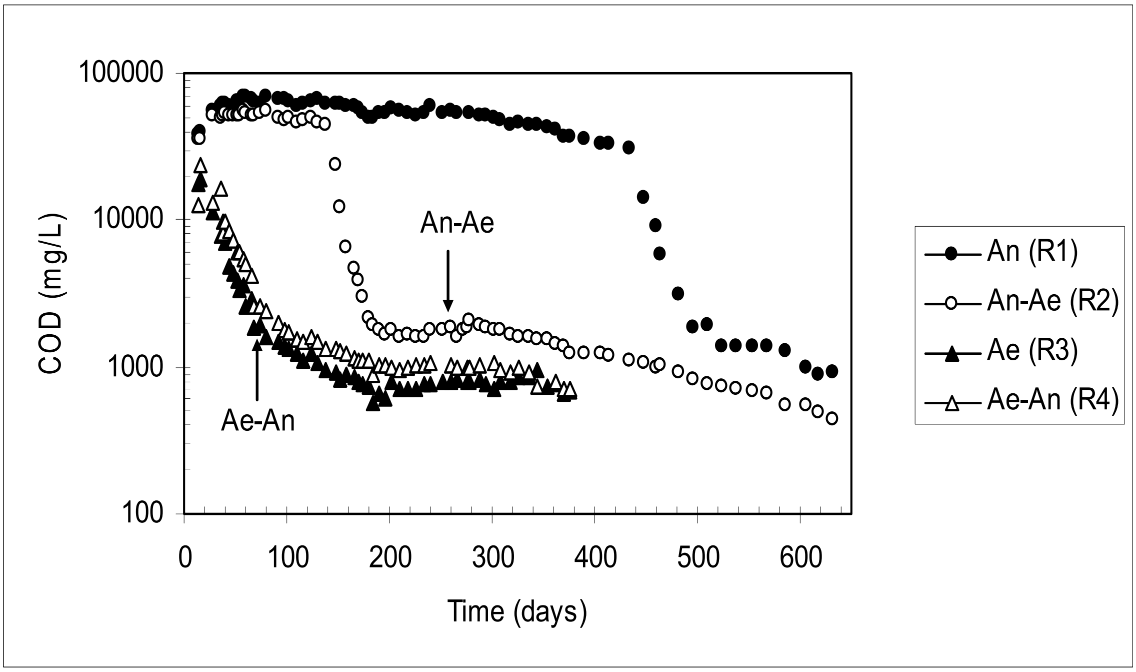

Figure 5.11. Leachate COD concentrations

The COD concentrations in Reactor 4 (aerobic to anaerobic) increased sharply from 12,608 mg/L to 23,569 mg/L as a result of rapid release of organics from the solid waste into leachate and dissolution of the organic acids and then started to decrease as a consequence of air addition. The COD concentration on Day 78 after the conversion of Reactor 4 from aerobic to anaerobic was 2,424 mg/L and lowered slowly to 707 mg/L on Day 374.

Landfilled wastes are dominated by organic material comprising (typically) 50% cellulose, 15% lignin, 10% hemicellulose, 5% protein as well as starch, pectin, and other soluble sugars (Barlaz, 1992). Cellulose is the most important carbon source for methanogenesis in landfills, however it is not an easily biodegradable material under anaerobic conditions. In fact, cellulose and hemicellulose, whose half-lives are about 15 years, contribute to 90% of total methane produced (Swarbrick, 2001). Hydrolysis of these complex organics in the presence of oxygen enhance biodegradation rate and convert to organic carbon in the waste mass to mostly carbon dioxide and water, with stabilized humic material remaining. Waste decomposition takes place within a few years under aerobic and controlled conditions instead of several decades (Hudgins and Harper, 1999). The results of the present study confirmed those of previous studies and indicated that approximately 90% of COD removal was completed by 72 days for Reactors 3 and 4 operated under aerobic conditions and by 135 days for Reactor 2 and by 462 days for Reactor 1 (anaerobic reactor), respectively.

It is important to note that aeration enables significantly faster biodegradation of organic matter. The results of the present study are similar to the findings of Cossu et al. (2003), who reported high COD values in the anaerobic reactor (20,000 mg/L) compared to the aerobic reactor (800 mg/L) after 120 days of operation. Carbon conversion by means of measuring the success of the aeration of the waste mass has been investigated by Ritzkowski et al.(2006). They observed a considerable reduction in leachate COD and TOC concentrations after approximately 20 days of aeration.

5.3.7.1. Mass Calculation of Chemical Oxygen Demand (COD). As indicated in Figure 5.11, data obtained for the COD measured in the study were reported in terms of concentration. While concentration provides an indication of the nature of chemical environment within the landfills, it does not give an adequate measure of the total mass of COD produced and/or removed in leachate. More correctly, COD production should encompass both the mass of COD transferred to leachate and the mass of COD transformed into gas especially methane under anaerobic conditions. The mass of COD transferred to the leachate should include both the leachate removed from the reactor for sampling and/or wasting and the leachate retained in the reactor in excess of field capacity. Therefore, variations in mass not only reflect changes in chemical and biological activity, but also the impact of such physical factors as evaporation, dilution and sampling. The mass of COD produced can be determined by performing a mass balance around the reactor control volume as shown in Figure 5.12. The mass of COD recirculated in the reactors is considered internal to the reactor control volume. The mass balance is performed as follows:

$$dM/dt = INFLOW - OUTFLOW + PRODUCTION - UTILIZATION \qquad (5.9)$$

The change in COD mass per unit time (dM/dt) is a function of the mass of COD added, removed, produced and consumed. The mass COD accumulated from one sampling period to the next will be negligible in comparison with the mass of COD utilized, lost in the effluent, or recycled. Thus, dM/dt can be assumed to be zero. Therefore:

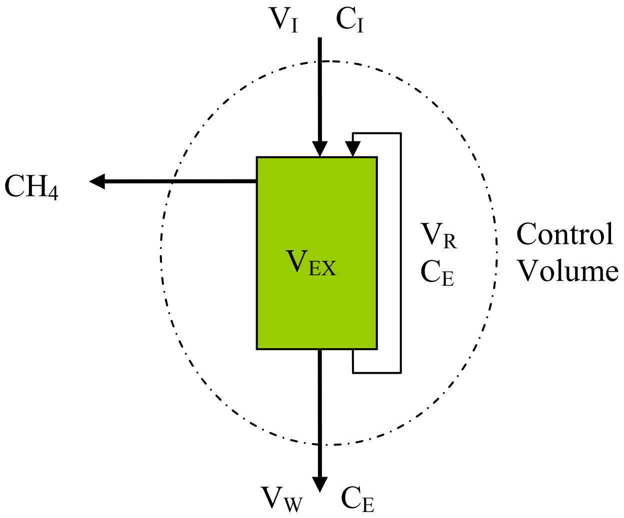

Figure 5.12. Mass balance on simulated landfill reactor control volume

$$0 = [V_I(i)*C_I(i)] - ([V_W(i)*C_E(i)] + [[C_E(i-1) + C_E(i)]/2 *V_{EX}(i)]) + M_{PRO}(i) - M_{UTIL}(i) \qquad (5.10)$$

i= sampling time period

M_{PRO}= Mass of COD produced (g)

M_{UTIL}= Mass of COD transformed into methane (g)

C_I=Concentration of COD incoming (g/L)

C_E=Concentration of COD in leachate sample (g/L)
V_I = Volume of water input to reactor (L)
V_W =Volume of leachate wasted (L)
V_{EX}= Volume of leachate in excess of field capacity (L)

The third term in the above equation represents an average concentration of COD in liquid retained in the reactor in excess of field capacity, because the assumption of a uniform concentration throughout the reactor is not necessarily valid. Equation can be further simplified because only distilled water was added to each reactor. Thus the input concentration, C_I, was zero. Rearranging the equation yields:

$$M_{PRO}(i)= [V_W(i)*C_E(i)] + [[C_E(i-1)+ C_E(i)]/2 *V_{EX}(i)] + M_{UTIL}(i) \qquad (5.11)$$

The first two terms in the equation represent the mass of COD released into the leachate, and the last term, $M_{UTIL,}$ is the mass of COD transformed into methane and calculated only for anaerobic degradation processes.

In order to determine M_{UTIL}, the volume of methane produced by each reactor was calculated. Because methane exists in both gaseous and dissolved forms, the volume of gaseous methane was calculated as follows (Pohland, 1993):

$$V_{MG}(i) = V_{GAS}(i)*F_{CH4}(i)*(273.15/(273.15 +T))*(1-VP/101.325) \qquad (5.12)$$

$V_{MG}(i)$ =Volume of methane gas produced (L)
V_{GAS} = Total volume of gas produced (L)
VP=Water vapor pressure at 32 °C (4.75 kN)
F_{CH4} = Fraction of methane in gas
T=Temperature = 32°C

The last two terms in this equation are a correction of the gas volume produced to standard temperature (0°C) and pressure (1 atm). The volume of dissolved methane was calculated by assuming that methane behaves as an ideal gas and that the density of water does not change significantly with temperature. Thus,

$V_{DM}(i) = F_{CH4}(i)*(1-4.75/101.325)/4,63x10^4*55.6 \text{ mol } H_2O/L*R*(273.15 + T)*V_{EX}(i)$(5.13)

R=Universal gas constant (1,987 kcal/kmol*K)
T=Temperature = 32°C
The total volume of methane produced (V_{CH4}) was determined as:

$V_{CH4}(i) = V_{MG}(i) + V_{DM}(i)$ (5.14)

The volume of methane produced can be converted to COD using the following equation

1 g COD=0.35 L CH_4 at 0°C and 1 atm then (Speece, 1995);

$COD_{CH4} = V_{CH4}(i)*(2.857 \text{ g COD/L } CH_4)$ (5.15)

The mass of COD produced in each reactor was calculated and results are presented graphically in Figures 5.13, 5.14, 5.15 and 5.16. The figures indicate the mass of COD released into leachate as well as the the total mass of COD transformed into methane gas. An increase in the mass of COD released occurred with the progression of the acid formation phase of Reactor 1 operated under anaerobic conditions. The mass of COD released declined concomitantly with the production of methane and resulting utilization of these available organics. COD in leachate were effectively removed by conversion to methane in Reactor 1 on Day 449. After this time, methane continued to be produced, suggesting that COD were still being generated. However, they were utilized as quickly as they were released, thus COD were difficult to detect in the leachate. Towards the end of the experimental period on Day 580, COD began to appear along with methane. The appearance of these organics probably resulted from degradation of more microbially resistant materials. Reactor 2 indicated similar behaviour with Reactor 1 and COD mass was significantly reduced by Day 150. After conversion of Reactor 2 from anaerobic to aerobic conditions on Day 264, the mass of COD released into leachate remained relatively constant until the end of study. A delay in the removal of COD from Reactor 1 compared to Reactor 2 was due to the inhibition of the decomposition of organics.

Reactor 3 exhibited a fast decline in the mass of COD released until Day 72, followed by a slight decline due to the stabilization of organics. Reactor 4 also displayed similar behaviour throughout the aerobic operation until Day 72. After the conversion of the Reactor 4 from aerobic to anaerobic conditions, COD were utilized as quickly and converted to methane and then a negligible mass of COD transformed into methane and, relatively constant mass of organics released to leachate.

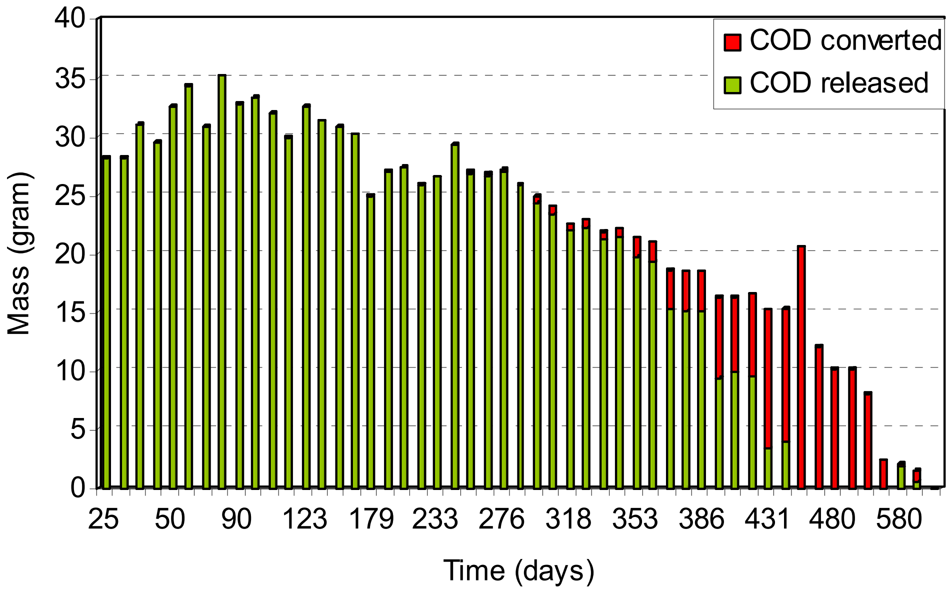

Figure 5.13. Mass of COD released and converted in Reactor 1

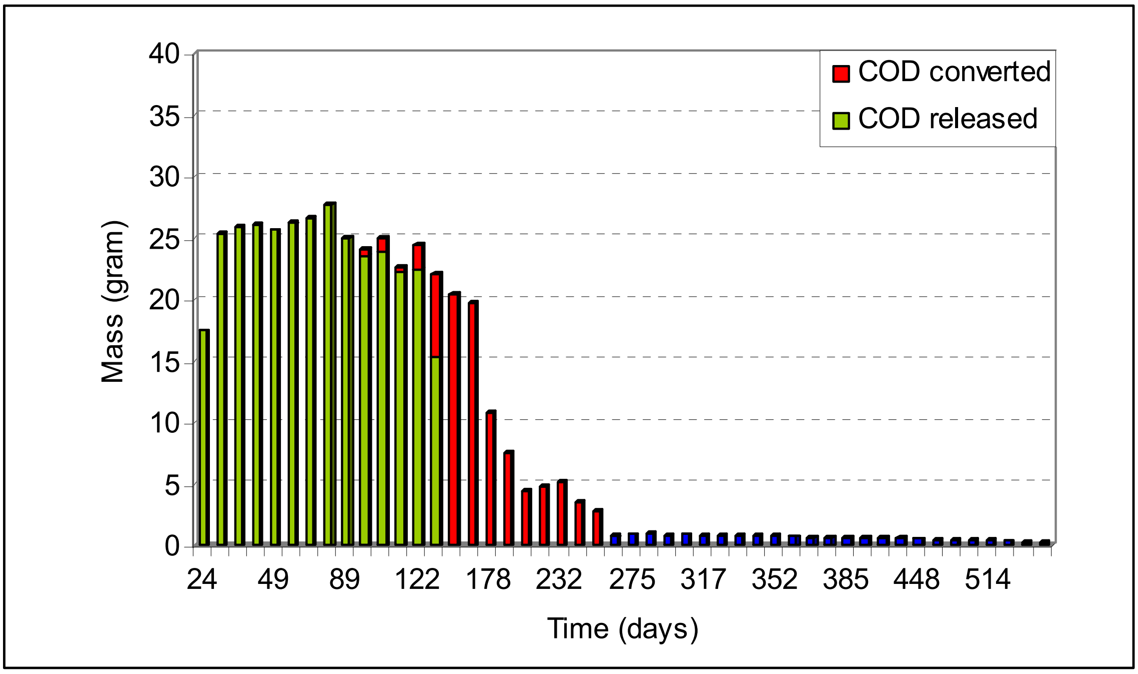

Figure 5.14. Mass of COD released and converted in Reactor 2

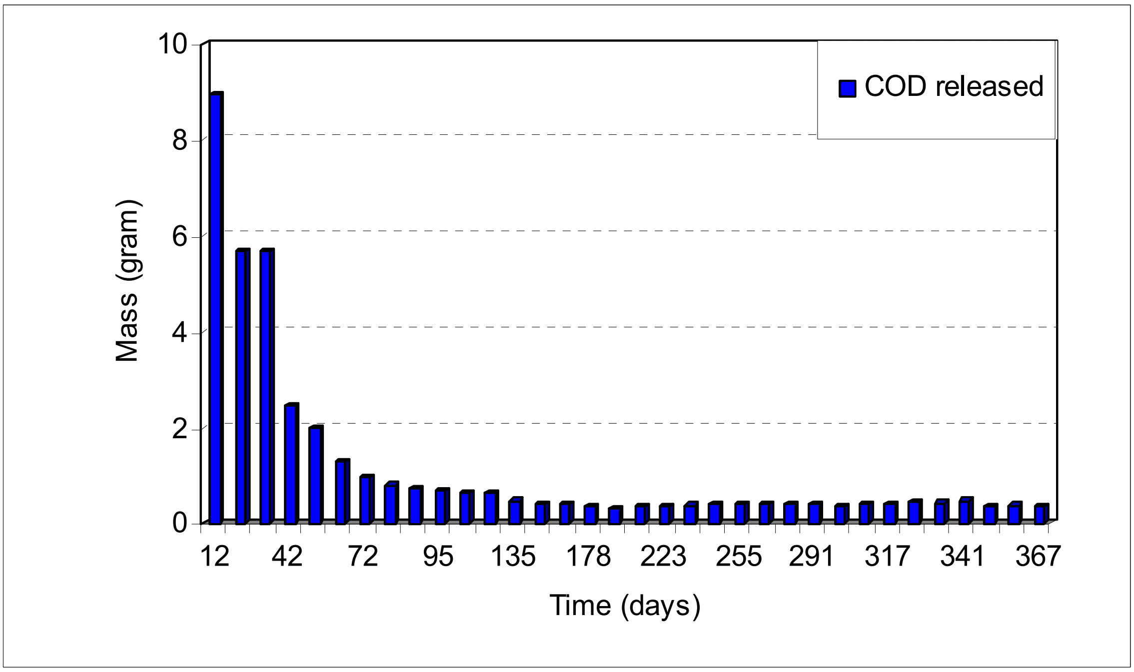

Figure 5.15. Mass of COD released and converted in Reactor 3

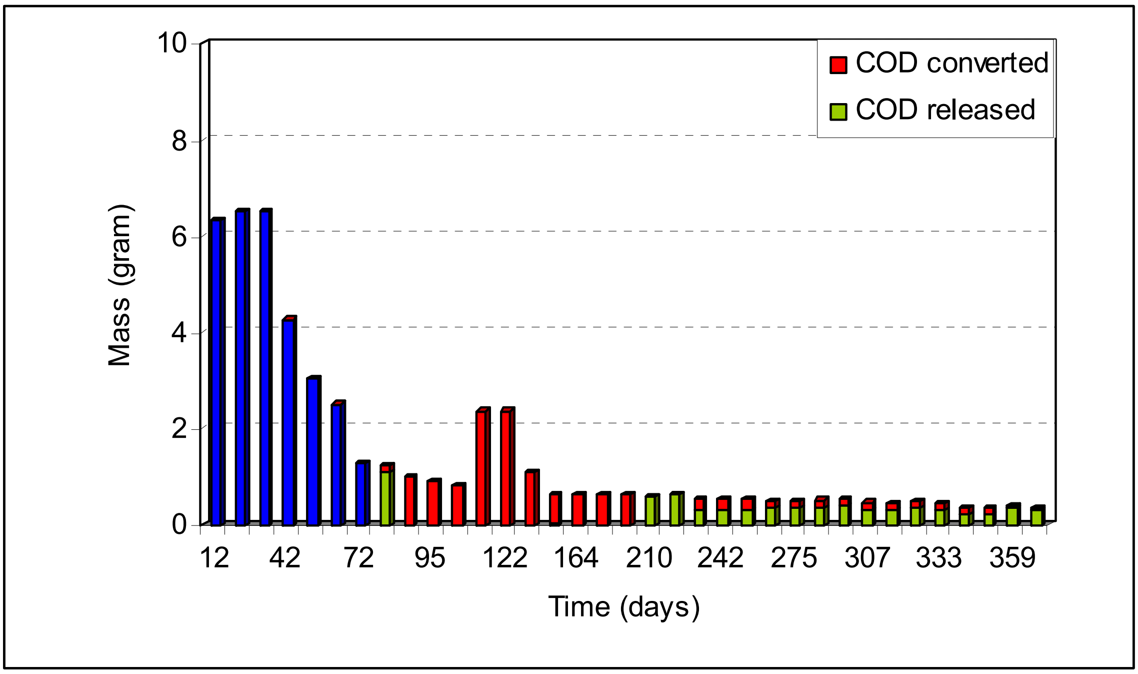

Figure 5.16. Mass of COD released and converted in Reactor 4

5.3.7.2. Kinetics of Chemical Oxygen Demand (COD) Removal. The results indicated that after the hydrolysis step (solubilization of organic matter), the COD degradation in leachate could be expressed by first-order kinetics. In the hydrolysis step, COD concentrations of the reactors increased due to conversion of composite organic matter to soluble organics. Besides, kinetic study does not include acid formation phase in the reactors within anaerobic process because it is the rate limiting step in this study and does not fit the selected kinetic model. After these assumptions, first order kinetics are expressed in the usual form:

$$dC/dt=-kC \qquad (5.16)$$

where,

C = the concentration of COD at any time (mg/L)

t= the time (days)

k= the reaction rate constant (days^{-1})

Then the apparent decay rate constants of organics for each reactor were calculated using MATLAB R2007a “Curve Fitting Toolbox”. The results of calculations are given in

Figures 5.17, 5.18, 5.19, 5.20 and summarized in Table 5.4. The results indicate that the rate constants of Reactors 1 and 2 under anaerobic conditions are higher than Reactors 3 and 4 under aerobic conditions. However, it is important to note that although the reaction rate constants were higher in anaerobic reactors, the total degradation time is much longer as a result of longer lag phase period. Catalini and Cossu (1999) also reported kinetic constant which were calculated for COD from mechanical-pretreated waste was 0.056 d^{-1}

Table 5.4. Apparent decay rate constants and statistical parameters

	REACTOR 1	REACTOR 2	REACTOR 3	REACTOR 4
k (day^{-1})	**0.0476**	**0.0524**	**0.0392**	**0.0268**
R^2	0.9855	0.9346	0.9573	0.8698
SSE	1.2926	2.3265	3.5212	1.4001
Adj. R^2	0.9843	0.9311	0.9566	0.8673
RMSE	997.2	3499	800.1	1641

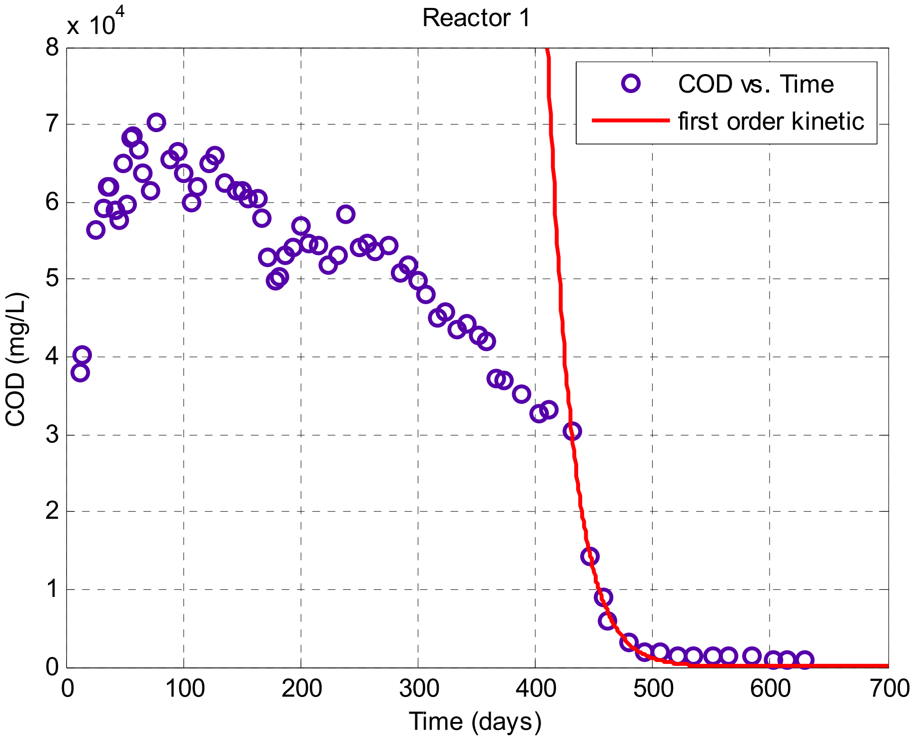

Figure 5.17. Determination of reaction rate constant (k) for Reactor 1

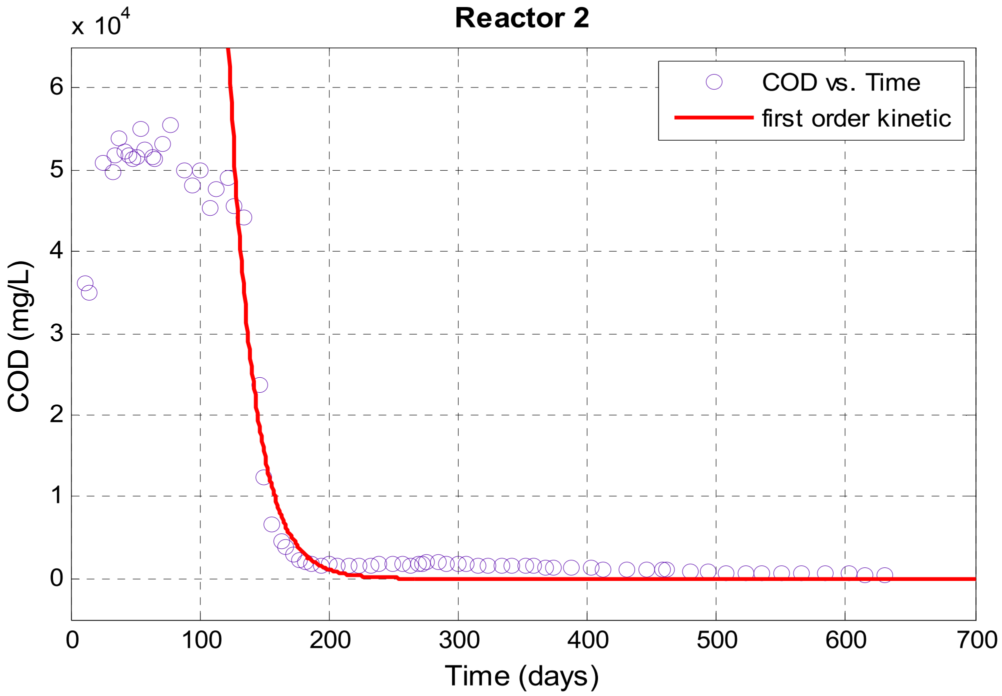

Figure 5.18. Determination of reaction rate constant (k) for Reactor 2

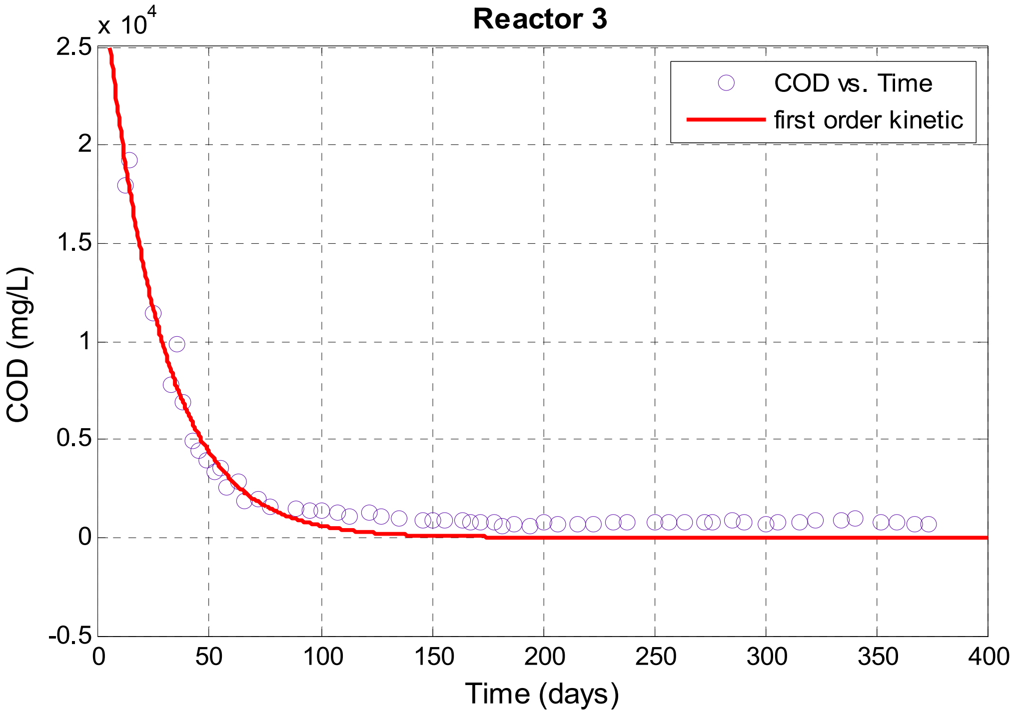

Figure 5.19. Determination of reaction rate constant (k) for Reactor 3

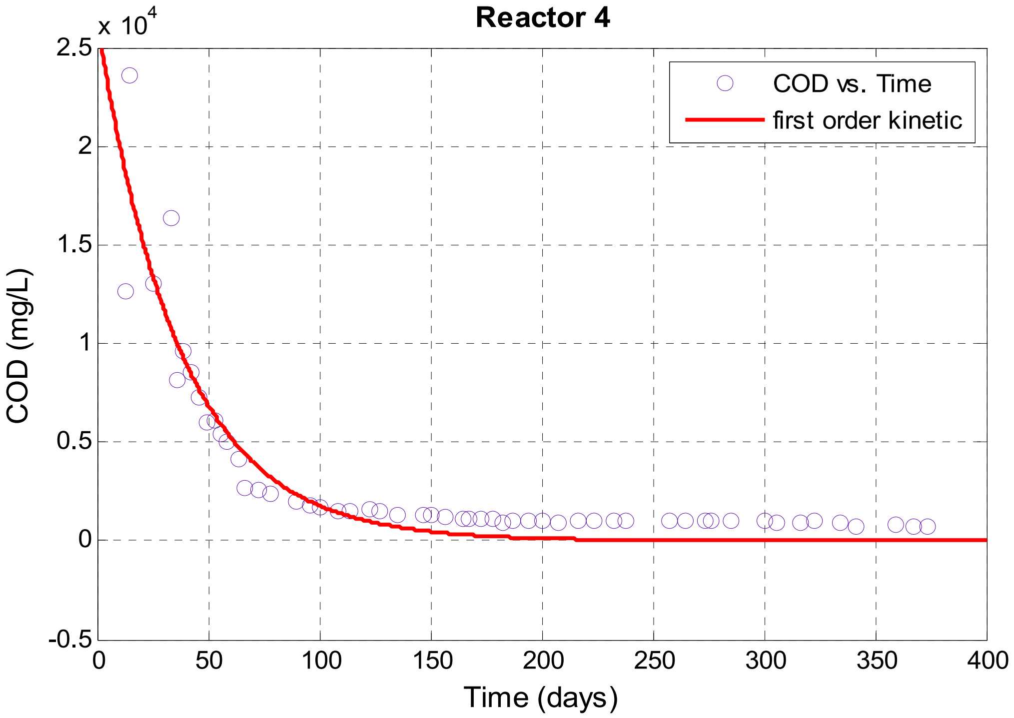

Figure 5.20. Determination of reaction rate constant (k) for Reactor 4

All statistical parameters are provided in Table 5.4. As evident from Table 5.4, R^2 values are in the range 0.87–0.99; good fit was obtained between measured data and the model simulations. With the aim of reevaluating this fit, the sum of squares due to error (SSE), R-square, and adjusted R-square and root mean square errors (RMSE) associated with the output model results were calculated. SSE measures the total deviation of the response values from the fit to the response values. A value closer to zero indicates a better fit. R-square measures how successful the fit is in explaining the variation of the data. If the number of fitted coefficients in model increases, R-square might increase although the fit may not improve. To avoid this situation, degrees of freedom adjusted R-square statistic should be used. This uses R-square statistic, and adjusts it based on the residual degrees of freedom. RMSE statistic is also known as the fit standard error and the standard error of the regression. Smaller RMSE indicates good fitness. Therefore, RMSE values of Reactors 3 and 1 are better fit for more useful prediction when compared to Reactors 2 and 3.

5.3.8. Total Organic Carbon (TOC)

TOC includes a variety of organic compounds, including humic and fulvic acids, VOAs and carbohydrates. Leachate TOC concentrations as a function of time in the reactors are presented in Figure 5.21. TOC concentrations showed similarity with COD concentrations (Fig. 5.11). Initial TOC concentration in Reactor 1 was determined as 17,990 mg/L. The accumulation of carbon dioxide in the reactor caused increases in TOC concentrations through anaerobic degradation. TOC concentration in the anaerobic reactor (Reactor 1) increased to a maximum of 27,380 mg/L on Day 70 and then decreased to 12,000 on Day 433 in accordance with the progression of microbially mediated stabilization processes. Onset to methanogenic conditions were confirmed by the increase in gas production and high methane content in the biogas and leachate TOC concentrations declined to 290 mg/L on Day 630.

In Reactor 2, TOC concentrations initially increased from 15,495 to 21,000 mg/L. The rapid decrease in TOC concentration from 18,260 mg/L on Day 122 to 474 mg/L on Day 187 was accompanied with the increase in methane concentration from 38 percent to 48 percent on Day 234. After the aeration started on Day 264, TOC concentrations declined slowly to 177 mg/L by the end of Day 630.

In the aerobic reactor (Reactor 3), as a result of rapid release of organics from the solid waste into leachate, TOC concentrations decreased from 1,438 mg/L on Day 28 to 218 mg/L on Day 374. Leachate TOC concentrations in Reactor 4 indicated the same decreasing trend with Reactor 3, reducing from 2,621 mg/L to 705 mg/L on Day 72 before conversion from aerobic to anaerobic conditions and to 220 mg/L at the end of the study.

It is possible to achieve high level of degradation of organic matter (80% of total degradation) within 66 days of operation in Reactor 3 (aerobic), 77 days in Reactor 4, 156 days in Reactor 2 and 458 days in Reactor 1 (anaerobic).

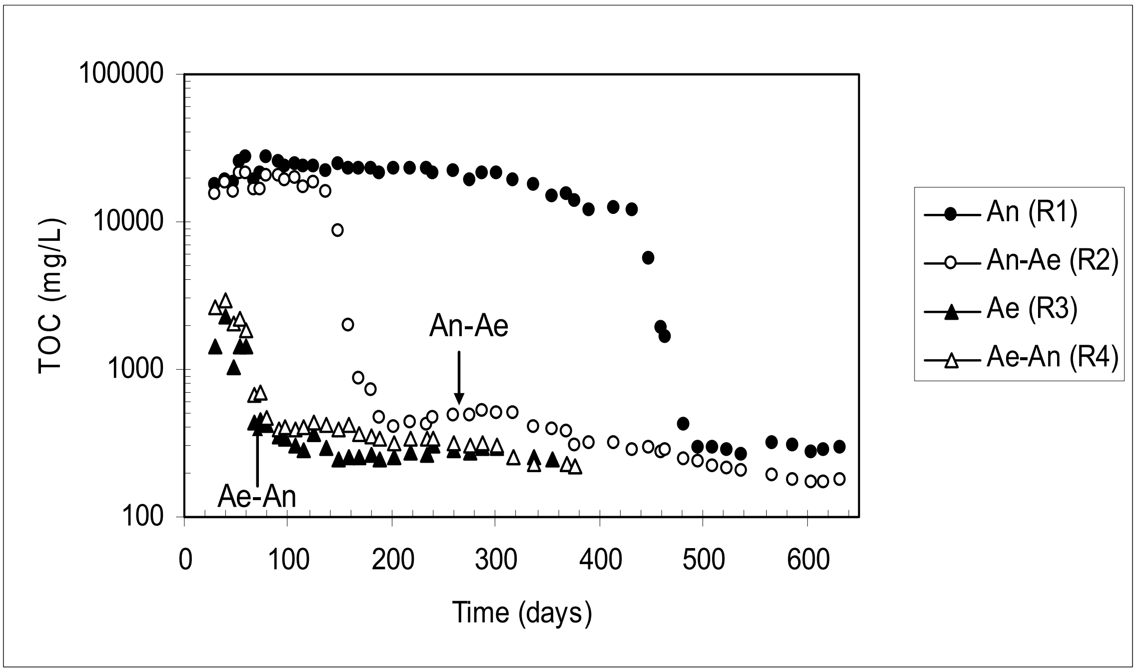

Figure 5.21. Leachate TOC concentrations

5.3.9. Volatile Fatty Acids

Volatile Fatty Acids (VFAs) are products of degradation and fermentation of organic fractions in the waste materials. The production and accumulation of VFAs is an indicator of the acid formation phase of a landfill. Acetic, proponic, isobutyric, butyric, isovaleric, valeric, isocaproic, caproic and heptanoic acids are among those monitored and measured during the study. The total volatile fatty acids (TVFAs) represent the combination of individual volatile fatty acids, converted to an equivalent amount of acetic acid by adjusting for differences in molecular weight. Leachate total volatile fatty acid concentrations in Reactors 1 and 2 was expressed as acetic acid given in Figure 5.22.

At the beginning of the study, high leachate TVFA concentrations in Reactors 1 and 2 under anaerobic conditions were observed. TVFAs remained in the systems due to the decomposition and accumulation of the readily available organics in the waste matrix. The maximum TVFA concentrations in Reactors 1 and 2 were 26,822 and 31,378 mg/L as acetic acid, respectively. A rapid reduction in TVFA was observed during the initial methane phase as volatile organic acids were converted to carbon dioxide and methane.

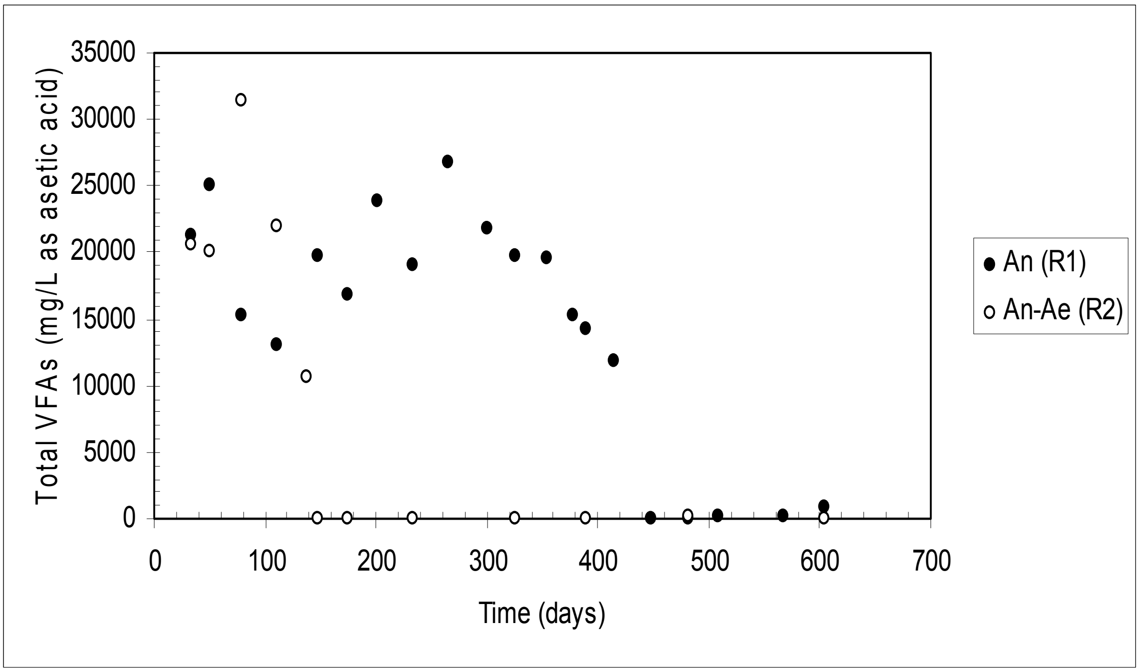

Figure 5.22. Leachate total volatile fatty acids in Reactors 1 and 2

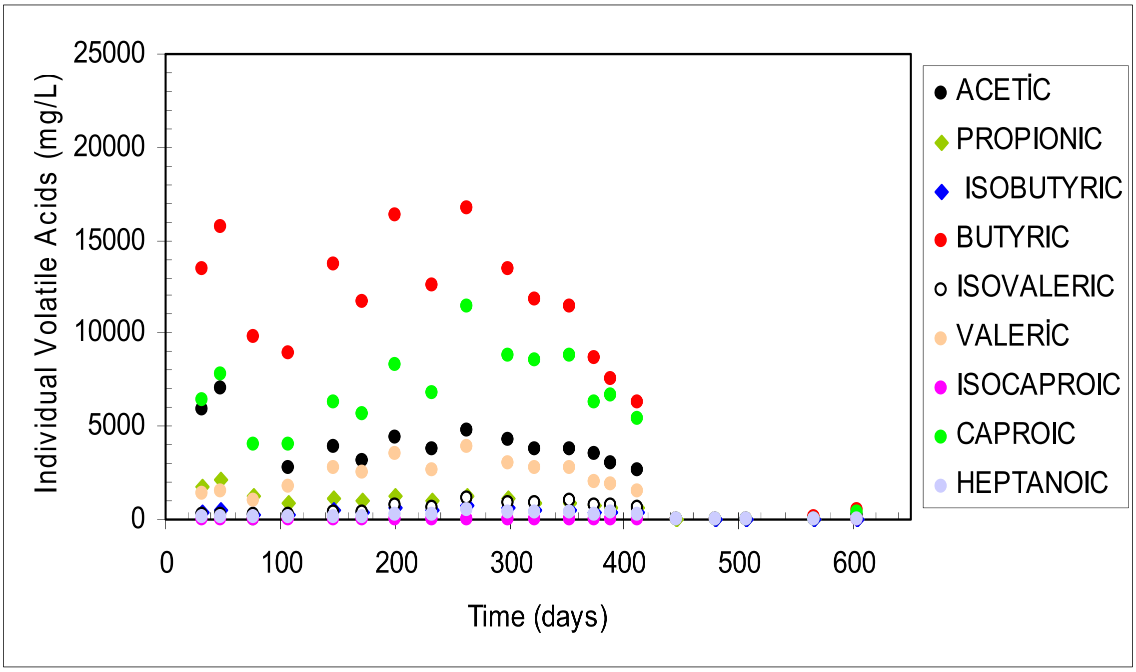

Figure 5.23 Leachate individual VFAs in Reactor 1

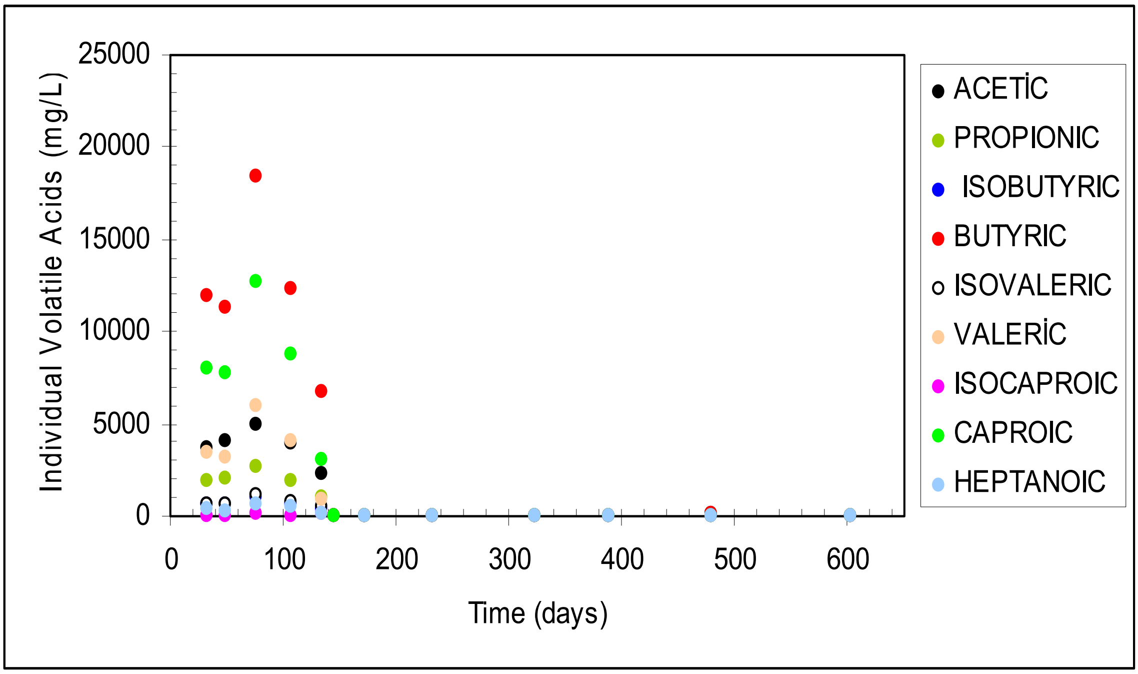

Figure 5.24. Leachate individual VFAs in Reactor 2

Correspondingly, high methane concentration and methane production were observed in the reactors.

The amount of the TVFA generated in Reactors 3 and 4 was insignificant due to rapid degradation of organics at the beginning when compared to the TVFA generated in Reactors 1 and 2 under anaerobic conditions. Leachate TVFA concentration in Reactor 4 did not exceed 100 mg/L as acetic acid the fact that the reactor was converted from aerobic to anaerobic conditions as readily biodegradable organics had been removed from the waste.

As Figures 5.23 and 5.24 indicate, the predominant species of volatile fatty acids detected in Reactors 1 and 2 were butyric, caproic and acetic acids, accounting for approximately 70% of the total volatile acids. On the other hand, Table 5.5 gives leachate individual VFAs in Reactors 3 and 4. Here, leachate individual VFA concentrations are insignificant due to partially stabilization of the waste.

Table 5.5. Leachate individual VFAs in Reactors 3 and 4

Reactors	Days	Acetic Acid (mg/L)	Propionic Acid (mg/L)	Butyric Acid (mg/L)	Caproic Acid (mg/L)
Reactor 3	32 (initial)	44	1	6	-
	374 (final)	3	-	-	-
Reactor 4	32 (initial)	33	1	-	-
	110	40	2	65	14
	374 (final)	27	2	-	-

The presence of higher molecular weight acids, such as butyric and caproic acids was consistent with the possibility of condensation reactions between shorter chain volatile acids. Similar results were reported by McCarty and cowerkers (1963a and b) using laboratory-scale digesters investigating the formation of caproic acid from butyric and acetic acids, and by Pohland and Kim (2000) interms of interruption of the requisite symbiotic relationship between the hydrogen oxidizing methanogens and aceticlastic fermentors with hydrogen and intermediary volatile acids and their condensation products accumulating at low pH during acid formation. This relationship is also emphasized by the redox reactions presented in Table 1.6 where condensation reactions are thermodynamically most favorable for the accumulation of higher acid homologous such as butyric and caproic acids as excess hydrogen shifts the equilibrium to the left and reserves the reaction preference. In addition, longer chain organic acids (propionate and above) also accumulate when the rate of hydrolytic and fermentative activity exceeds the rate of acetogenic conversion of fermentation intermediates to acetate and hydrogen.

5.3.10. Biochemical Oxygen Demand (BOD)

BOD_5 indicated similar trend with COD and TOC removal (Fig. 5.25). Initial BOD_5 concentrations were 40,800 mg/L in Reactor 1, 37,800 mg/L in Reactor 2, 5,100 mg/L in Reactor 3 and 7,050 mg/L in Reactor 4. In the reactors under anaerobic conditions, BOD_5 concentrations increased to a maximum of 48,000 mg/L in Reactor 1 and 39,300 mg/L in Reactor 2 due to the hydrolysis of organic material. After reaching maximum concentrations, decreasing trend in the values from both reactors were observed as a result of the enhancement of the utilization of organic material by microorganisms. BOD_5 concentration of Reactor 1 decreased to 25,200 mg/L on Day 433, 163 mg/L on Day 537 and reached to 55 mg/L at the end of the experiment. BOD_5 concentrations in Reactor 2 declined sharply from 31,950 mg/L on Day 129 to 72 mg/L on Day 252 due to the increased activity of microorganisms after the onset of methanogenic conditions and then were observed between 68 and 6 mg/L after the conversion of the reactor from anaerobic to aerobic conditions on Day 264.

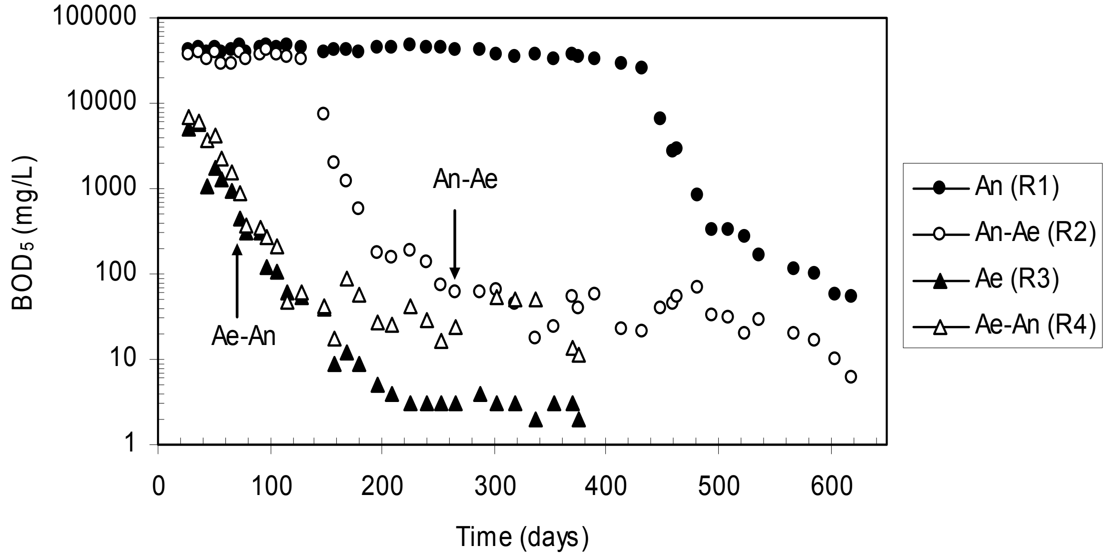

Figure 5.25. Leachate BOD_5 concentrations

Leachate BOD_5 concentrations of Reactors 3 and 4 under aerobic conditions decreased very rapidly. These sharp decreases were supported by the decrease in COD and TOC concentrations. The high rate of BOD_5 utilization by aerobic microorganisms also caused these sharp decreases. High initial BOD_5 concentration in the aerobic reactor (Reactor 3) decreased to 62 mg/L on Day 113. This decrease continued until day 223 and then, BOD_5 concentrations stayed at a constant value of about 3 mg/L. A similar decline was observed in Reactor 4 under aerobic degradation due to the same operational conditions. However, when compared to Reactor 3, it can be seen (Figure 5.25) that leachate BOD_5 of Reactor 4 was higher under anaerobic conditions after Day 77 since utilization of BOD_5 by anaerobic microorganisms is lower than aerobic ones.

To sum up, BOD_5 concentrations of the aerobic reactors (Reactors 3&4) decreased rapidly while BOD_5 concentrations of the anaerobic reactors (Reactors 1&2) decreased slowly followed by rapid reduction after the onset of methanogenic conditions. Rapid reductions in TOC and BOD_5 in the aerated landfill bioreactor showed the feasibility of stabilization of MSW.

BOD_5 to COD ratio is often used to assess the biodegradability of the organic matter in leachate, and thus to understand the degree of landfill stabilization (Alvarez-Vazquez et al., 2004). BOD decreases more rapidly than COD over time since COD includes the recalcitrant organic compounds. Consequently, as waste ages, the ratio between BOD and COD decreases. In old stabilized landfills, the BOD_5/COD ratio is below 0.10 (Kjeldsen et al., 2002). A low BOD_5/COD suggests that leachate is low in biodegradable organic carbon and relatively high in hard-to-biodegrade organic matter such as humic compounds. In this research, initial high BOD_5/COD ratio decreased from 0.57 to 0.03 at the end of experiment in the aerobic reactor (Reactor 3) (Fig. 5.26). BOD_5/COD ratio in Reactor 4 was initially 0.77 and reduced to 0.36 towards conversion from aerobic to anaerobic conditions. After the conversion, BOD_5/COD ratio stayed at higher values when compared to Reactor 3 and reached to 0.02 in the end. On the other hand, relatively high BOD_5/COD ratios were obtained from the reactor under anaerobic conditions. Initial BOD_5/COD ratio of anaerobic reactor (Reactor 1) was about 0.72, and release of organics increased this ratio to 0.89–0.93 after Day 200 after which it decreased to 0.45 at around Day 460, finally reaching 0.05 at the end of experiments. The values proposed by Kjeldsen et al. (2002) were 0.58 and 0.06 for the acid phase and the methanogenic phase, respectively. BOD_5/COD ratio in Reactor 2 was initially 0.74 and then increased to a maximum of 0.88 on Day 97. After conversion from anerobic to aerobic conditions, the BOD_5/COD ratio of Reactor 2 did not change much due to the nearly completed stabilization. The ratio was about 0.04 on Day 263 and decreased to 0.01 until the end during the aeration. Borglin et al. (2004) found that BOD_5/COD ratio of aerobic and anaerobic landfill bioreactors were 0.03 and 0.45, respectively, after 365 days.

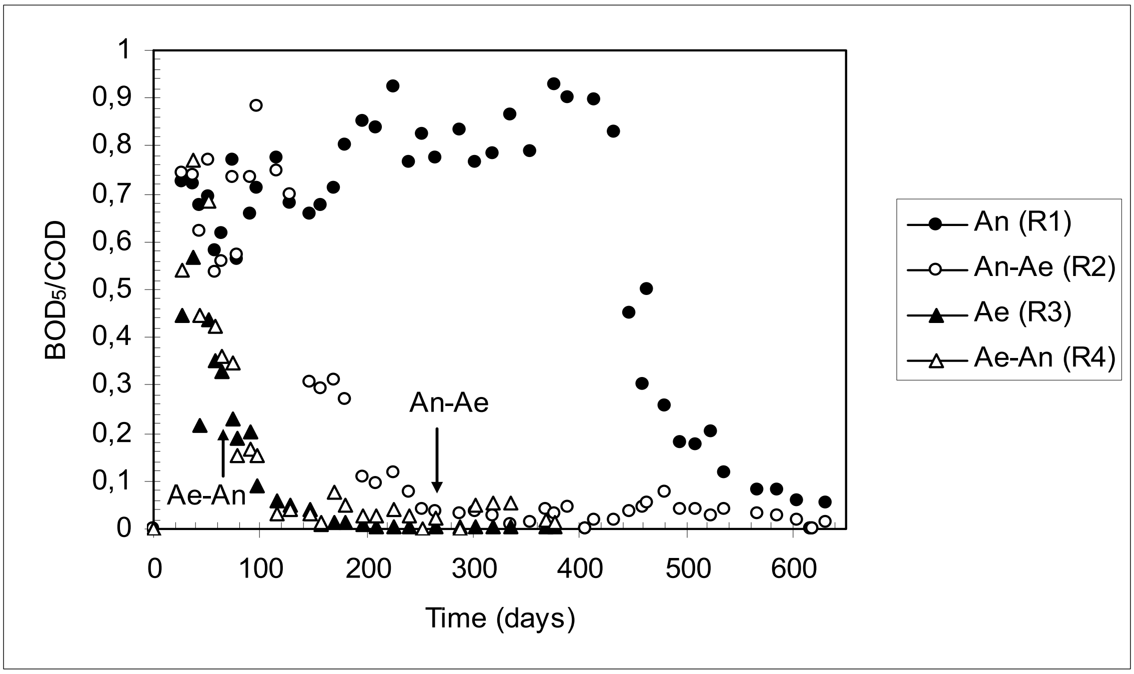

Figure 5.26. Leachate BOD_5/COD ratios in the reactors

5.3.11. Total Solid (TS)

Total solid (TS) and total volatile solid (TVS) concentrations in leachate from all bioreactors are presented in Figure 5.27 and Figure 5.28, respectively. The change in TS and TVS exhibited similar trend with COD variation. The initial leachate TS concentrations of reactors were 55,346 mg/L for Reactor 1, 47,500 mg/L for Reactor 2, 10,150 mg/L for Reactor 3 and 9,165 mg/L for Reactor 4. Similarly, the initial TVS concentrations were 38,562 mg/L for Reactor 1, 33,240 mg/L for Reactor 2, 3,575 mg/L for Reactor 3 and 4,150 mg/L for Reactor 4. During the experimental period, it was observed that TS and TVS concentrations of leachate showed a decreasing trend because of dilution (washout) and decomposition of the waste under aerobic and anaerobic conditions. At the end of the study, TS concentrations of leachate of Reactors 1,2,3 and 4 were 3212 mg/L, 3228 mg/L 6353 mg/L and 5116 mg/L, respectively.

Like TS concentrations, TVS concentrations in Reactors 1 and 2 under anaerobic conditions decreased as a function of time and declined sharply from 13,030 mg/L on Day 388 to 1,360 mg/L on Day 507 (Reactor 1) and from 14,250 on Day 145 to 1,757 on Day 232 (Reactor 2) after the onset of methanogenic conditions. As the methanogenic bacteria started to consume the organic matter in leachate to produce new cells, methane and carbon dioxide, the TVS concentration declined to low values at the end of experiments. These values were 1,060 mg/L for Reactor 1 and 784 mg/L for Reactor 2 on Day 630. On the other hand, TVS concentrations in Reactors 3 and 4 declined in the time and reached to 1310 mg/L and 1190 mg/L, respectively at the end of study.

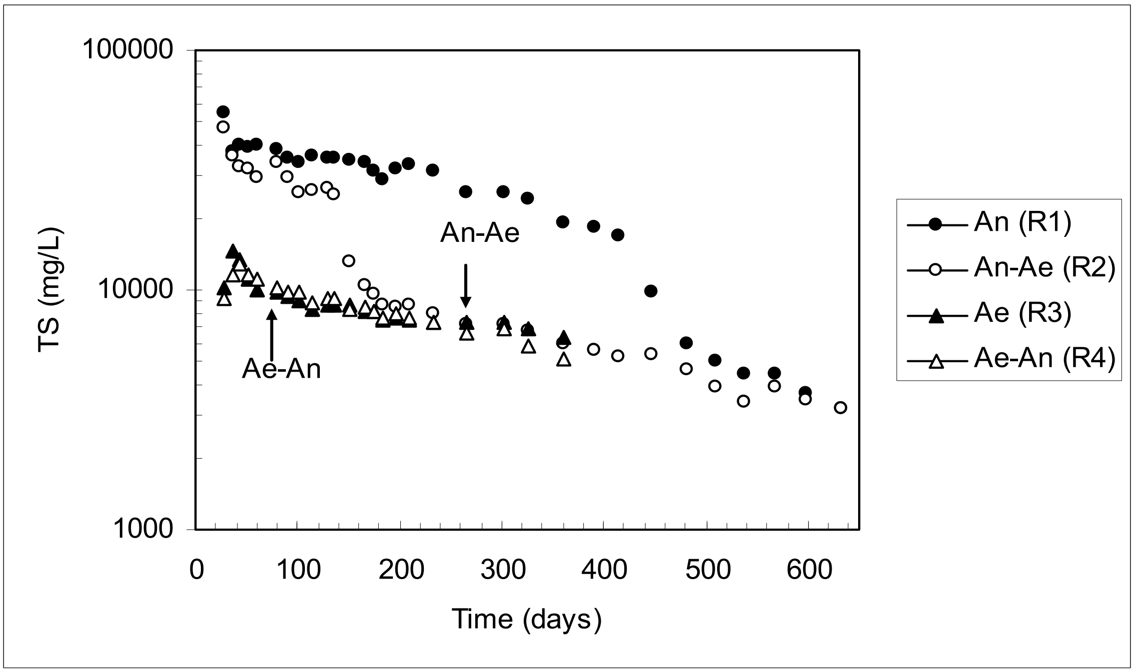

Figure 5.27. Leachate TS concentrations

The organic compounds in leachate decrease more rapidly than the inorganics with increasing age of the landfill. The decrease of organics is due to decomposition and washout while the inorganics decrease due to washout, filtration, precipitation and/or sorption within the landfill mass. TVS/TS ratio was used to understand the amount of the organic matter in leachate. In the anaerobic degradation, TVS/TS ratio increased initially in the reactors due to the increase of organic matter in the leachate which is the end product in the hydrolysis and acidogenic steps. As the methanogenic bacteria started to consume the organic matter in leachate to produce new cells, methane and carbon dioxide, the TVS/TS ratio decreases at the end of the experiments. In the aerobic stage, aerobic bacteria consumed the organic matter in leachate to produce carbon dioxide and new cells and TVS/TS ratio declined as a function of time.

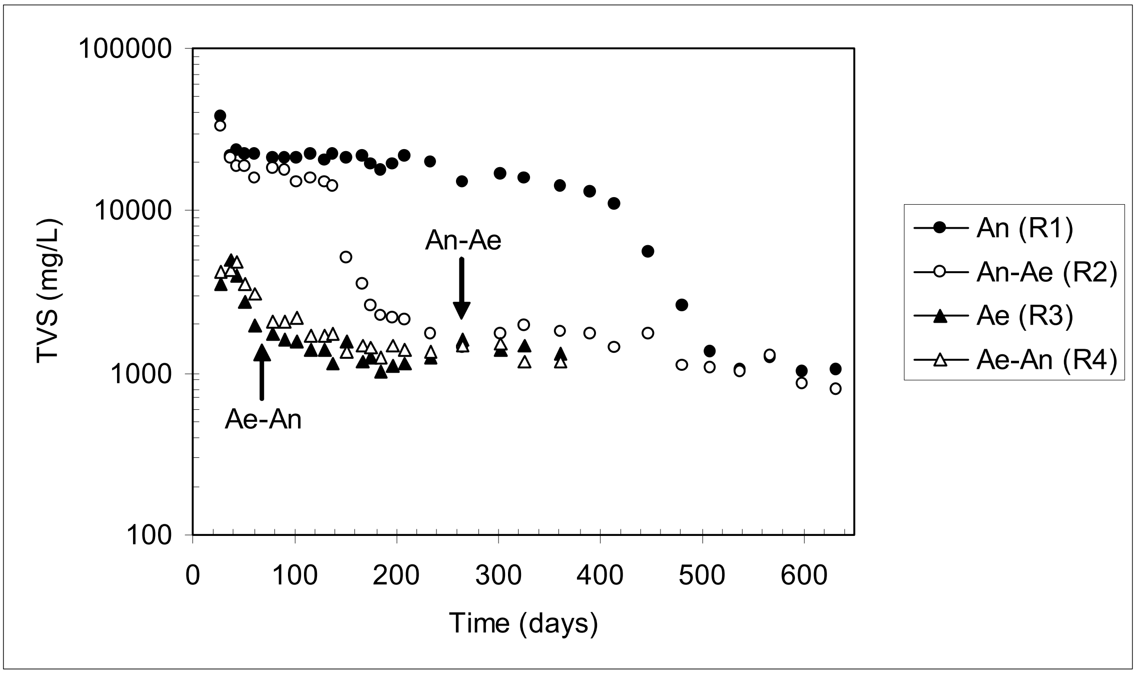

Figure 5.28. Leachate TVS concentrations

In this research, relatively high TVS/TS ratios were obtained from the anaerobic reactors (Fig. 5.29). Initial TVS/TS ratio was about 0.70, and release of organics increased this ratio to 0.75 in Reactor 1 on Day 359. TVS/TS ratio decreased to 0.45 at around day 480, finally reaching 0.25 at the end of experiments. In Reactor 2, TVS/TS ratio ranged between 0.54 and 0.70 until day 135 and then decreased to 0.25 at the end of experiment. On the other hand, initial high TVS/TS ratio decreased from 0.45 to 0.2 at the end of experiment in the aerobic reactors.

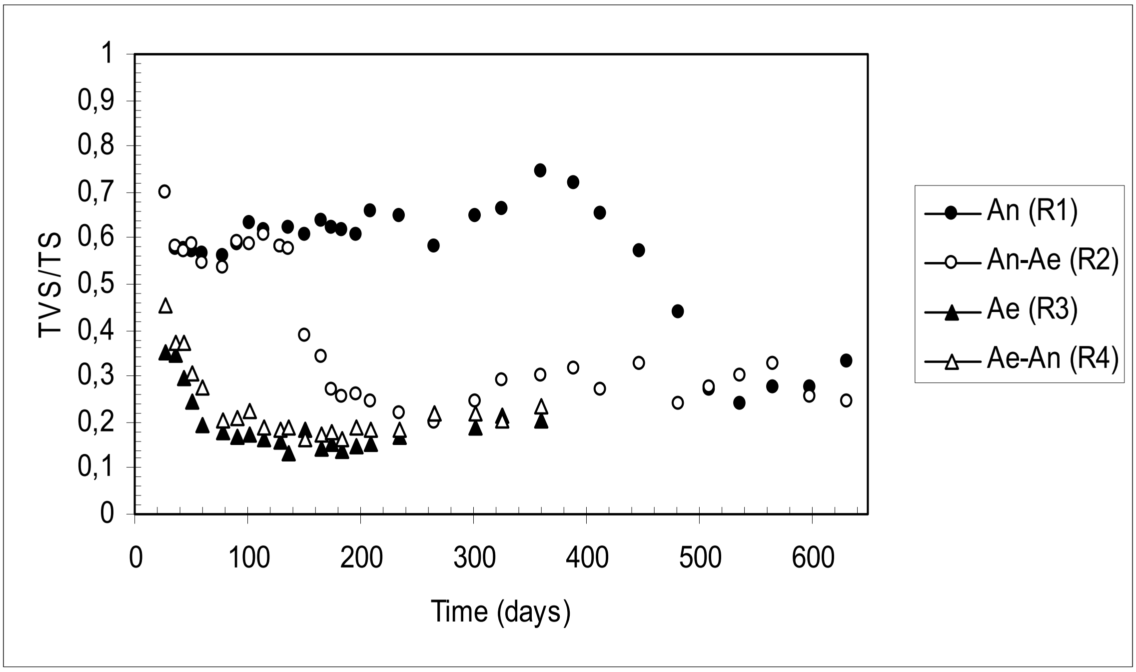

Figure 5.29. Leachate TS/TVS in the reactors

5.3.12. Total Suspended Solid (TSS)

Total suspended solids (TSS) include all particles suspended in water that will not pass through a filter. Suspended solids come from clay and silt, fine particles of organic matter, inorganic particulates (such as iron), soluble coloured compounds in leachate. The biomass concentration can also be adequately described by volatile suspended solids (VSS). Volatile suspended solids evaluation does not distinguish between living cells, dead biomass and nonviable organic particles. In the case of MSW leachate, VSS occurred to be completely useless to biomass determination. Suspended solid (SS) and volatile suspended solid (VSS) concentrations in leachate samples from all bioreactors are presented in Figure 5.30 and Figure 5.31, respectively.

Initally, SS and TVS values increased due to the leachate recirculation. While SS concentrations of Reactors 1 and 2 reached to about 3600 mg/L and 3000 mg/L respectively, SS concentrations of Reactors 3 and 4 rised to approximately 2200 mg/L and 2500 mg/L, respectively. It was observed fluctuations in the reactors in terms of SS and TVS concentrations during the first 200 days. These fluctuations contributed to the increases in turbidity values. At the end, SS concentrations of the reactors decreased to 296 mg/L for Reactor 1, 84 mg/L for Reactor 2, 127 mg/L for Reactor 3 and 117 mg/L for Reactor 4. Similarly, volatile suspended solids (VSS) indicated parallel decreasing trend (Figure 5.31) and dropped to 294 mg/L for Reactor 1, 82 mg/L for Reactor 2, 120 mg/L for Reactor 3 and 116 mg/L for Reactor 4.

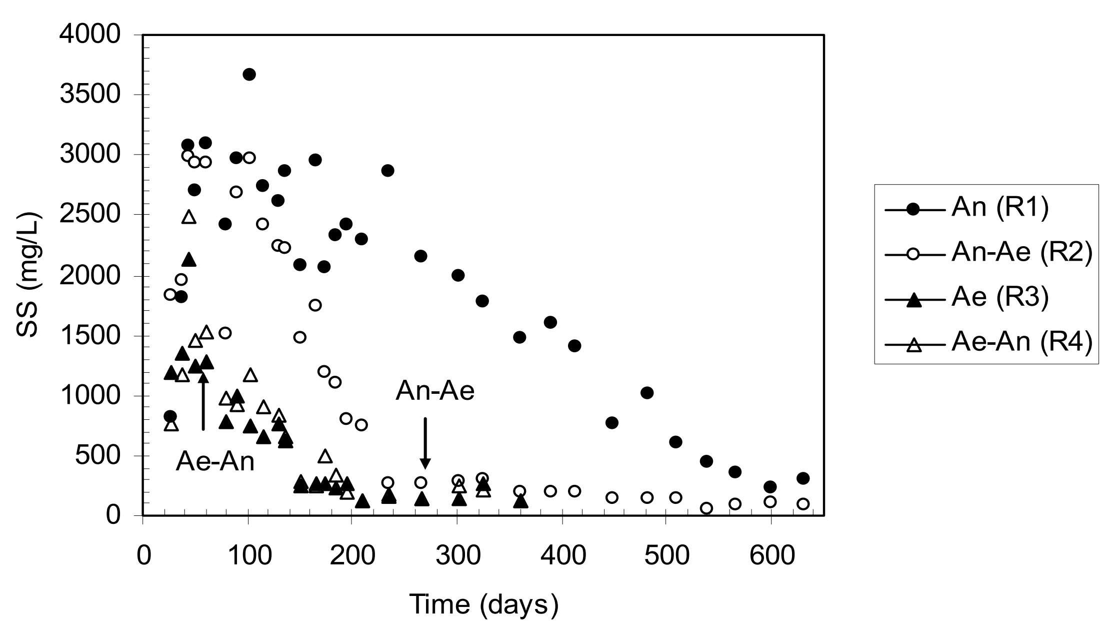

Figure 5.30. Leachate SS concentrations

In anaerobic reactors where acidogenic phase prevails VSS amount increased due to the formation of VFAs. In Figure 5.31, where VSS values of the leachate samples were sketched, Reactors 1 and 2 under anaerobic conditions have very high values. After the onset of methanogenic conditions, VSS values declined rapidly. On the other hand, VSS values of Reactors 3 and 4 decreased earlier due to the acceleration of waste degradation under aerobic conditions.

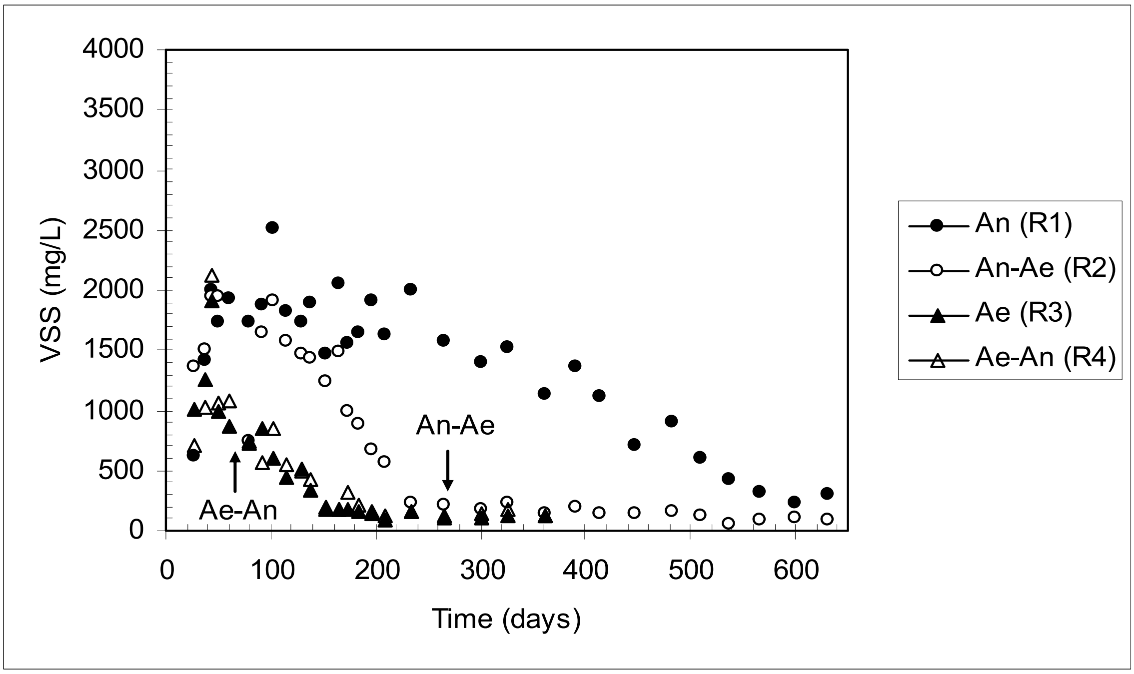

Figure 5.31. Leachate VSS concentrations

5.3.13.Total Dissolved Solids (TDS)

High conductivity values of the Reactors (5.25–23.70 mS/cm) indicated the presence of dissolved inorganic materials. This is also apparent from the corresponding high TDS (total dissolved solids) values, which reflect the extent of mineralization during decomposition of the waste in the landfill. TDS is a measure of the concentration of dissolved constituents in water, which commonly include carbonate, bicarbonate, chloride, sulfate, phosphate, nitrate, calcium, magnesium, sodium, organic ions, and other ions. TDS consist of both organic and inorganic molecules and ions in leachate. Figures 5.32 and 5.33 present leachate dissolved solid (DS) and volatile dissolved solid (VDS) concentrations of the reactors.

DS and VDS concentrations of all reactors indicated similar decreasing trend caused by the dilution effect of water used for rainfall simulation. Initial DS and VDS concentrations were 35,967 and 19,813 mg/L for Reactor 1, 26,745 and 16,195 mg/L for Reactor 2, 7,560 and 2,700 mg/L for Reactor 3 and 7,010 and 2,935 mg/L for Reactor 4, respectively. These concentrations decreased to 2,544 and 672 mg/L for Reactor 1, 2,960

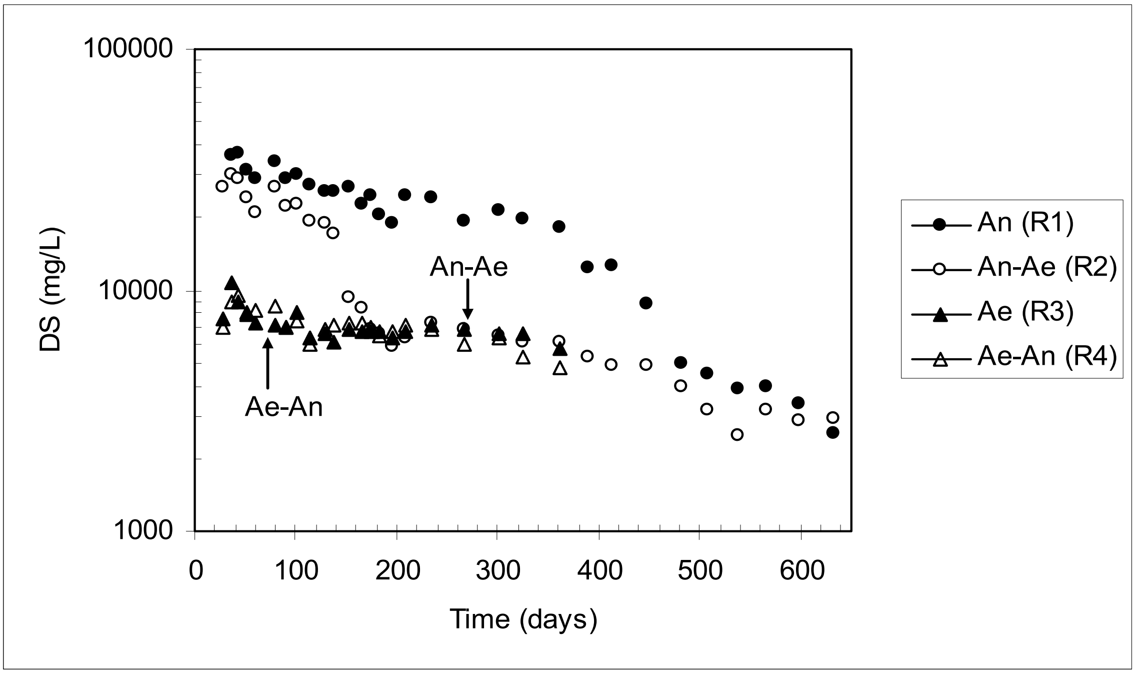

Figure 5.32. Leachate DS concentrations

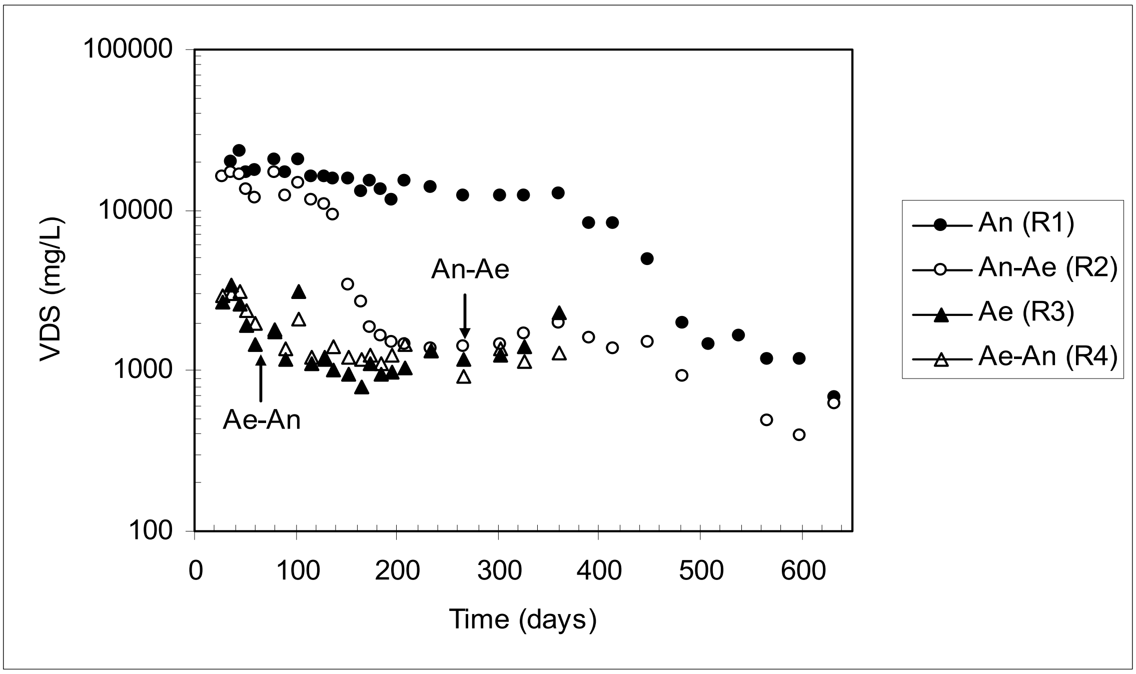

Figure 5.33. Leachate VDS concentrations

and 612 mg/L for Reactor 2 on Day 630 and 5,753 and 2,277 mg/L for Reactor 3 and 4,803 and 1,290 mg/L for Reactor 4 on Day 359, respectively. At the end, DS and VDS concentrations of the reactors operated initially under aerobic conditions (Reactors 3 & 4) were observed as higher compared to the concentrations of Reactors 1 and 2. This can be a result of the dilution effect and the washout because while the water addition into Reactors 1 & 2 was taken time for 630 days, the addition into Reactors 3 & 4 was done for only 374 days.

5.3.14. TKN and NH_3-N

Nitrogen which has a potential for water and soil pollution is another major constituent in leachate. Most of the nitrogen available in landfill bioreactors is in the form of ammonia nitrogen (NH_3-N) and is produced from the degradation of proteins and amino acids (Price et al., 2003). Some researchers reported that ammonia was the most significant long-term component of leachate (Christensen et al., 1998), because ammonia is stable under anaerobic conditions. The variations in leachate TKN and NH_3–N concentrations in all reactors are presented in Fig. 5.34 and 5.35, respectively.

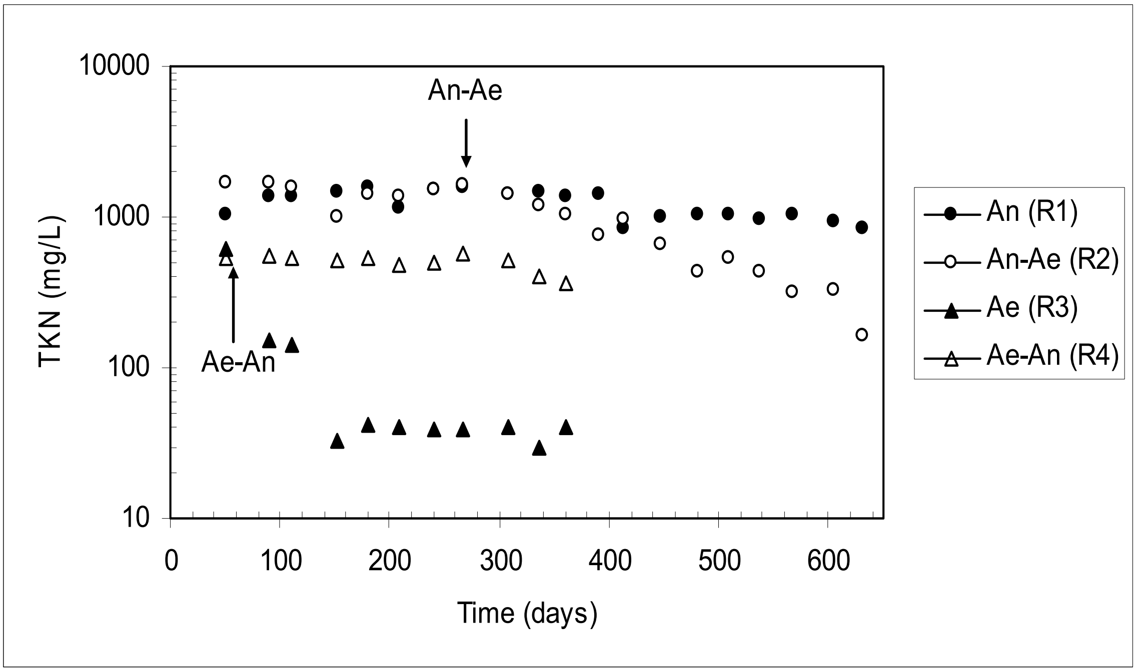

Figure 5.34. Leachate TKN concentrations

Initial concentrations of TKN and ammonia-nitrogen were found to be similar in the reactors. The leachate NH_3-N concentrations of the reactors increased rapidly at the beginning of study due to the degradation of organic nitrogenous compounds. Initial NH_3-N concentration increased from 390 mg/L to a maximum of 1064 mg/L for the anaerobic reactor (Reactor 1) and from 533 mg/L to 1604 mg/L for Reactor 2. TKN concentrations were between 840 and 1590 mg/L in Reactor 1 and between 162 and 1620 mg/L in Reactor 2. The leachate NH_3-N concentrations in Reactors 1 and 2 accumulated to a high level since there is no ammonia elimination process under the anaerobic conditions (Vigneron et al., 2007). After the operational conditions in Reactor 2 was converted from anaerobic to aerobic conditions on Day 264, NH_3–N concentration began to decrease and reached to 123 mg/L on Day 630. TKN concentration of Reactor 2 was 162 mg/L at the end of experiment. On the other hand, NH_3-N and TKN concentrations of Reactor 1 were 660 and 840 mg/L at the end of study, respectively. In anaerobic systems, protein fraction of biodegradable wastes release ammonia-nitrogen and they may accumulate in the leachate to concentrations up to 1000–6000 mg/L (Burton and Watson-Craik, 1998, 2001; Calli et al., 2005a). The recirculation practice in the anaerobic reactor reintroduces ammonia to the system, keeping its value almost constant throughout experiment. Several researches indicated that NH_3-N is a significant long-term pollution problem in landfills (Burton and Watson-Craik, 1998; Onay and Pohland, 1998; Price et al., 2003; He et al., 2007). The increased ammonia concentrations intensify the toxicity of the leachate. Pohland et al. (1987) stated that concentrations between 200 and 1500 mg/L have shown to have no adverse effects on anaerobic process, concentrations ranging from 1500 to 3000 mg/L were shown to have inhibitory effects at higher pH levels, and concentrations above 3000 mg/L were very toxic. However Calli et al. (2005b) have shown that NH_3-N levels up to 6000 mg/L could be tolerated in the anaerobic bioreactors. In this study, NH_3-N concentrations in the anaerobic reactor do not reach inhibitory or toxic levels (Fig. 5.35).

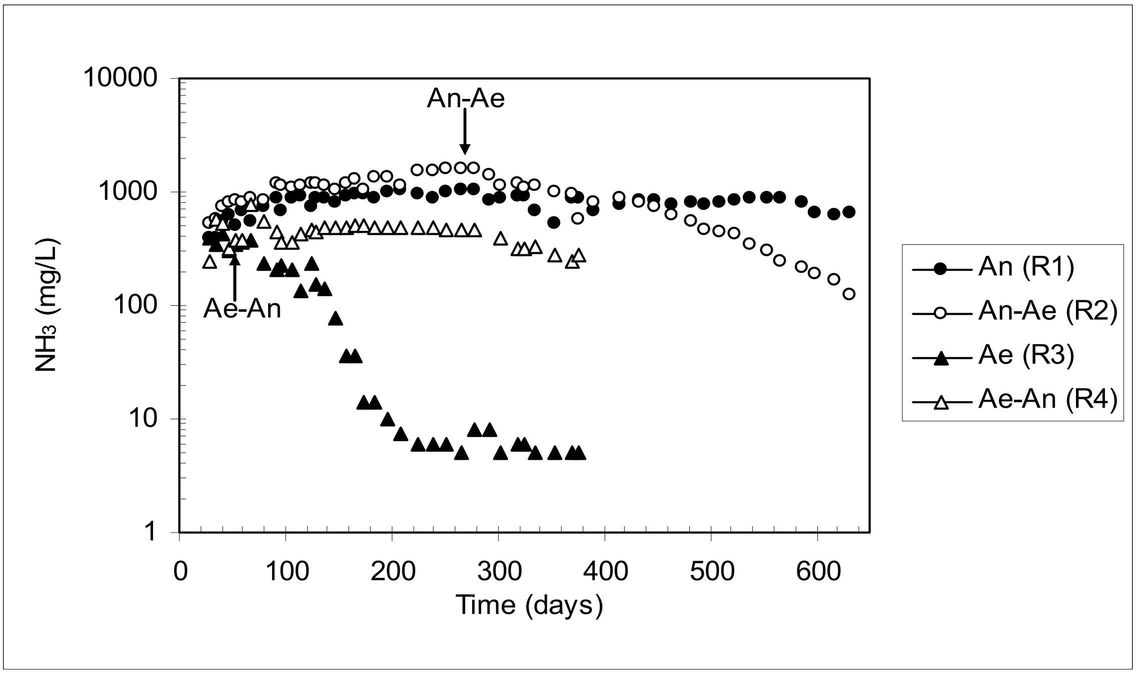

Figure 5.35. Leachate NH_3-N concentrations

On the other hand, under aerobic conditions, the ammonia-nitrogen is oxidized to nitrite and nitrate by nitrifying bacteria (nitrobacter and nitrosomonas). TKN and ammonia-nitrogen concentrations in leachate from the aerobic reactor (Reactor 3) indicated the same decreasing trend. Initial TKN and ammonia-nitrogen concentrations were measured as 620 and 399 mg/L, respectively. TKN concentration decreased to 140 mg/L on Day 108 and 42 mg/L on Day 178 and stayed constant throughout the study. NH_3-N concentrations, on the other hand, decreased to 132 mg/L on Day 116 and 14 mg/L on Day 175 and continued to decline slightly until reaching to 5 mg/L at the end. These results agree with the findings of Cossu et al. (2003), in which the ammonium concentration declined to 5–6 NH_3-N mg/L after 120 days of operation in the aerobic reactor. The possibility for ammonia to have been removed by air stripping was very low. With the leachate having a pH during the experiment of about 8, there was little prospect of removing nitrogen from the leachate by air stripping, since the optimum pH for ammonia stripping is between 10.8 and 11.3 (He and Shen, 2006). Thus, nitrogen attenuation in the aerobic bioreactor was mainly caused by biological conversion. Since the concentrations of nitrogen are reduced, the need for ex situ leachate treatment could also be reduced, depending on applicable regulations.

The TKN concentrations in Reactor 4 (aerobic to anaerobic) did not change during the experiment due to the conversion of the reactor from aerobic to anaerobic conditions. TKN concentrations were between 540 and 360 mg/L. NH_3-N concentrations increased from 242 mg/L to 773 mg/L on Day 66 and then began to decrease to 277 mg/L at the end of study. All these results indicate that an aerobic landfill bioreactor with leachate recirculation could effectively remove ammonia-nitrogen.

5.3.15. Total Phosphorus and Orthophosphate

The availability of nutrients is essential to the microbially mediated processes of landfill stabilization. Phosphorus is used to synthesize energy-storage compounds (adenosine triphosphate-ATP) as well as RNA and DNA. Phosphorus appears in leachate as orthophosphate (PO_4^{-3}), polyphosphate (P_2O_7) and organically bound phosphorus. Total phosphorus and orthophosphates were monitored as one of the major nutrients in both aerobic and anaerobic degradation. The daily variations in concentrations of total phosphorus and orthophosphate observed during the experimental period are presented in Figures 5.36 and 5.37.

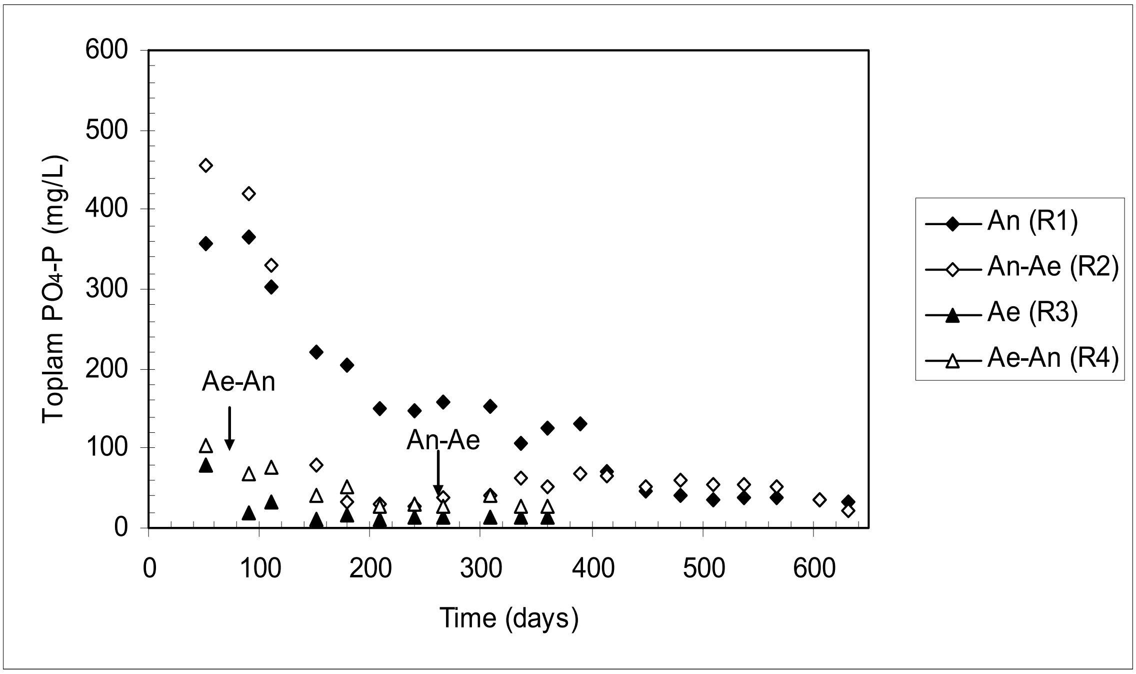

Figure 5.36. Leachate total phosphorus concentrations

Initial total phosphorus concentrations of leachate of Reactors 1,2,3,4 were 358 mg/L, 456 mg/L, 78 mg/L, 105 mg/L, respectively on Day 49. Similarly, initial orthophosphate concentrations of leachate from Reactors 1,2,3,4 were 168 mg/L, 358 mg/L, 250 mg/L, 127 mg/L respectively on Day 16. Total phosphorus and orthophosphate concentrations in the reactors followed similar attenuation trend throughout the experimental period. In the anaerobic reactors, orthophosphate concentrations increased to 410 mg/L for Reactor 1 and 520 mg/L for Reactor 2 on Day 33 due to hydrolysis of organic material and polyphosphates. After this day, decreasing trend in the values from both reactors was observed as a result of the enhancement of the utilization of orthophosphate by microorganisms and the dilution caused by water additions. Orthophosphate concentration of Reactor 1 decreased to 236 mg/L on Day 113, 82 mg/L on Day 216, 40 mg/L on Day 446 and reached to 25 mg/L at the end of the experiment. Orthophosphate concentrations in Reactor 2 declined sharply from 244 mg/L on Day 135 to 76 mg/L on Day 146 due to the increased activity of microorganisms after the onset of methanogenic conditions and then were observed between 67 and 20 mg/L after the conversion of the reactor from anaerobic to aerobic conditions on Day 264. On the other hand, the final total phosphorus concentrations of leachate of Reactors 1 and 2 decrased to 34 mg/L and 22 mg/L, respectively at the end of experiment.

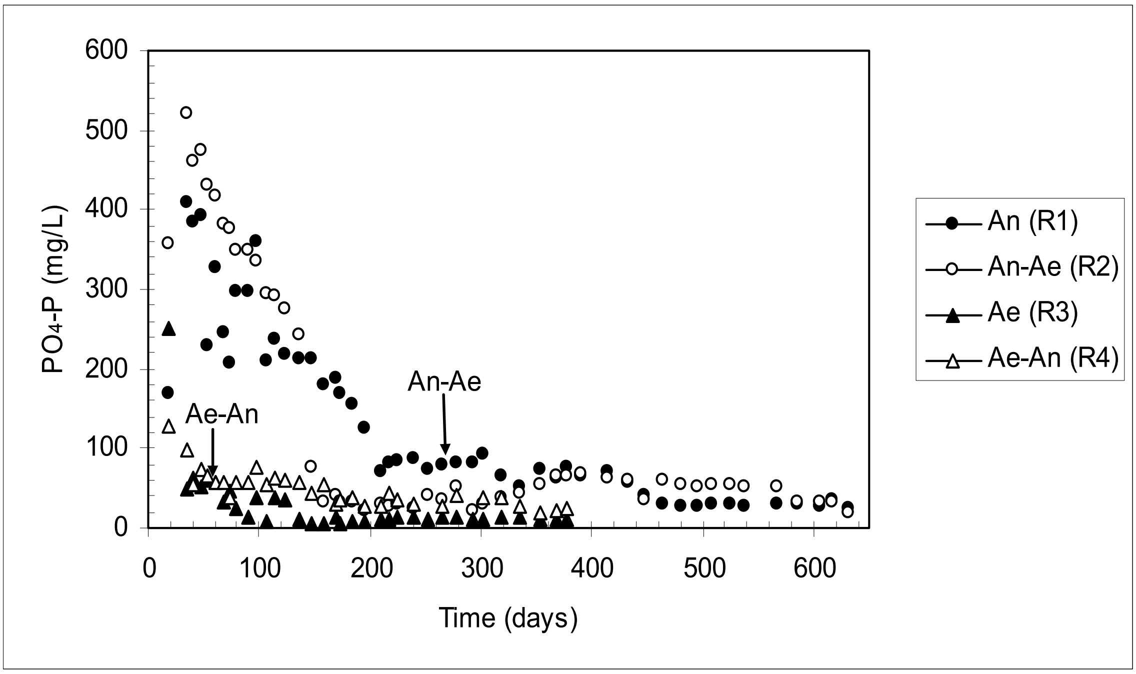

Figure 5.37. Leachate orthophosphate concentrations

Total phosphorus and orthophosphate concentrations of Reactors 3 and 4 under aerobic conditions decreased rapidly. These sharp reductions were supported by the decrease in COD concentrations. The high rate of orthophosphate utilization by aerobic microorganisms also caused these sharp decreases. High initial orthophosphate concentration in the aerobic reactor (Reactor 3) decreased to 50 mg/L on Day 33. This decrease continued until Day 200 and then, orthophosphate concentrations stayed at a constant value of about 12 mg/L. A similar decline was observed in Reactor 4 under aerobic degradation due to the same operational conditions. However, when compared to Reactor 3, it can be seen (Figures 5.36 and 5.37) that leachate total phosphorus and orthophosphate concentrations of Reactor 4 were higher under anaerobic conditions after Day 77 since utilization of phosphorus by anaerobic microorganisms is lower than aerobic ones. The C:N:P ratio listed in the literature as 250:5:1 to 500:5:1 for anaerobic and 100:5:1 for aerobic treatments (Metcalf and Eddy, 1991; Henze et al., 1995; Maier, 2000). For anaerobic treatment, the required nitrogen and phosphorous concentrations is lower than the case for aerobic treatment due to the fact that anaerobic treatment produces only 20% biomass compared to aerobic treatment. Total phosphorus concentrations of leachate from Reactors 3 and 4 decreased to 13 mg/L and 26 mg/L, respectively at the end of the experiments.

To sum up, phosphorus attenuation was attributed to microbial utilization, washout (dilution) and possible complexation reactions. Chemical precipitation of the phosphate anion (PO_4^{-3}) with Ca^{+2}, Al^{+3} or Fe^{+3} cations was also possible in the reactors. It may also be concluded that orthophosphate concentrations in the reactors were sufficient for aerobic and anaerobic degradation throughout the study.

5.3.16. Alkalinity

Alkalinity represents a capability of a system to buffer the effects of volatile acids which tend to depress the pH below the desired level. Alkalinity in leachate is due to carbonates, bicarbonates, borates, ammonia, organic bases, sulfides and phosphates. Adequate alkalinity, or buffer capacity, is necessary to maintain a stable pH in the digester for optimal biological activity. An alkalinity level ranging from 1,000 to 5,000 mg/L as

$CaCO_3$ was recommended by Tchobanoglous and Burton (1979). The measured alkalinity concentrations for the reactors are given in Figure 5.38.

The initial alkalinity concentrations were 5,768 mg/L as $CaCO_3$ in Reactor 1, 5,227 mg/L as $CaCO_3$ in Reactor 2, 3,219 mg/L as $CaCO_3$ in Reactor 3, 2,652 mg/L as $CaCO_3$ in Reactor 4. In anaerobic reactor (Reactor 1), leachate alkalinity varied between 5,500 and 7,500 mg/L as $CaCO_3$ and remained relatively constant which, along with high VFA concentrations and low pH (5.0 to 5.5), suggested that a volatile organic acid buffering system predominated during the acid formation phase. After transition to methanogenic conditions, pH values increased and total alkalinity concentrations tended to decrease because methanogens utilized the available VFA as substrate. Total alkalinity of the anaerobic reactor decreased to 3,800 mg/L as $CaCO_3$ at end of the experiment.

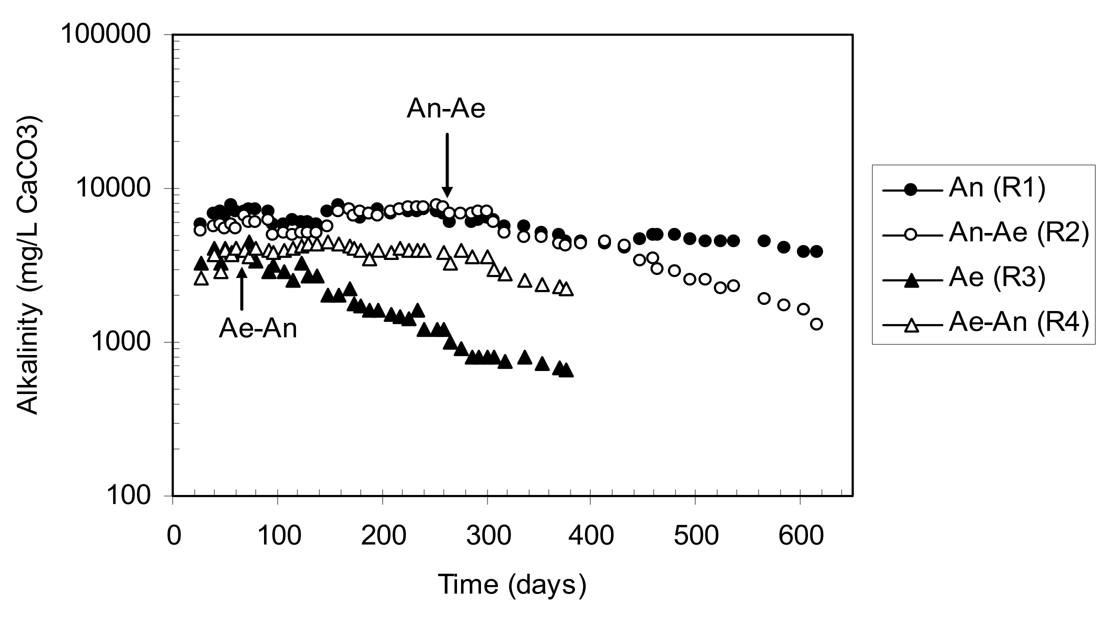

Figure 5.38. Leachate alkalinity concentrations

In Reactor 2 (anaerobic-aerobic), leachate alkalinity concentration varied between 5,000 and 7,800 mg/L as $CaCO_3$ under anaerobic conditions until Day 264. When compared to Reactor 1, it can be noticed (Figure 5.38) that leachate alkalinity concentrations of Reactor 2 were higher and enough to buffer volatile acids. After conversion of the reactor from anaerobic to aerobic conditions on Day 264, alkalinity reduction due to nitrification was observed until the end of experiment. Leachate alkalinity was 1,300 mg/L as $CaCO_3$ at the end of the experiments.

In the aerobic reactor (Reactor 3), leachate alkalinity first increased to its highest value of 4,500 mg/L as $CaCO_3$ and then began to decrease on day 77 and reached to 660 mg/L as $CaCO_3$ at the end of experiment. The pattern observed in alkalinity reduction corresponds to changes in ammonia and nitrate nitrogen concentrations observed for Reactor 3 over same period of time with an decrease in alkalinity with accumulation of nitrate. Studies indicated that 6-7.4 mg alkalinity as $CaCO_3$ is destroyed per mg ammonia nitrogen oxidized to nitrate (EPA,1975).

In Reactor 4 (aerobic-anaerobic), leachate alkalinity concentrations were between 2,652 and 4,150 mg/L as $CaCO_3$ during aerobic decomposition. After conversion of the reactor from aerobic to anaerobic conditions on Day 77, alkalinity in the leachate of Reactor 4 did not show significant change during study except the days towards the end of experimental period, alkalinity slightly declined to 2200 mg/L as $CaCO_3$ by Day 374.

5.3.17. Acidity

Acidity is a measure of the capacity of a water to neutralize strong base. This measurement is based on the total acidic constituent of a solution (strong and weak acids, hydolyzing salts, etc.). Carbon dioxide from biological oxidation of organic matter, sulfuric acid from sulfur, sulfides or iron pyrites, salts of heavy metals, particularly those with trivalent metal ions, such as Fe (III) and Al (III) and organic acids such as acetic acid, propionic acid and butyric acid contribute to acidity (Snoeyink and Jenkins, 1980). The measured acidity concentrations for the reactors are given in Figures 5.39.

The initial acidity concentrations were 5,850 mg/L as $CaCO_3$ in Reactor 1, 4,100 mg/L as $CaCO_3$ in Reactor 2, 213 mg/L as $CaCO_3$ in Reactor 3, 200 mg/L as $CaCO_3$ in Reactor 4. As can be seen Figure 5.39, acidity concentrations in anaerobic reactors were high due to organic acids whereas acidity in aerobic reactors were low as a result of CO_2 stripping by air. Acidity concentrations in the anaerobic bioreactors (Reactors 1 and 2) indicated decreasing trend as a function of time and declined sharply to 450 mg/L as $CaCO_3$ on Day 446 (Reactor 1) and on Day 146 (Reactor 2) after the onset of methanogenic conditions because methanogens utilized the available organic acids as substrate. At the end of study, acidity concentrations were 440 mg/L as $CaCO_3$ in Reactor 1, 200 mg/L as $CaCO_3$ in Reactor 2, 20 mg/L as $CaCO_3$ in Reactor 3, 200 mg/L as $CaCO_3$ in Reactor 4.

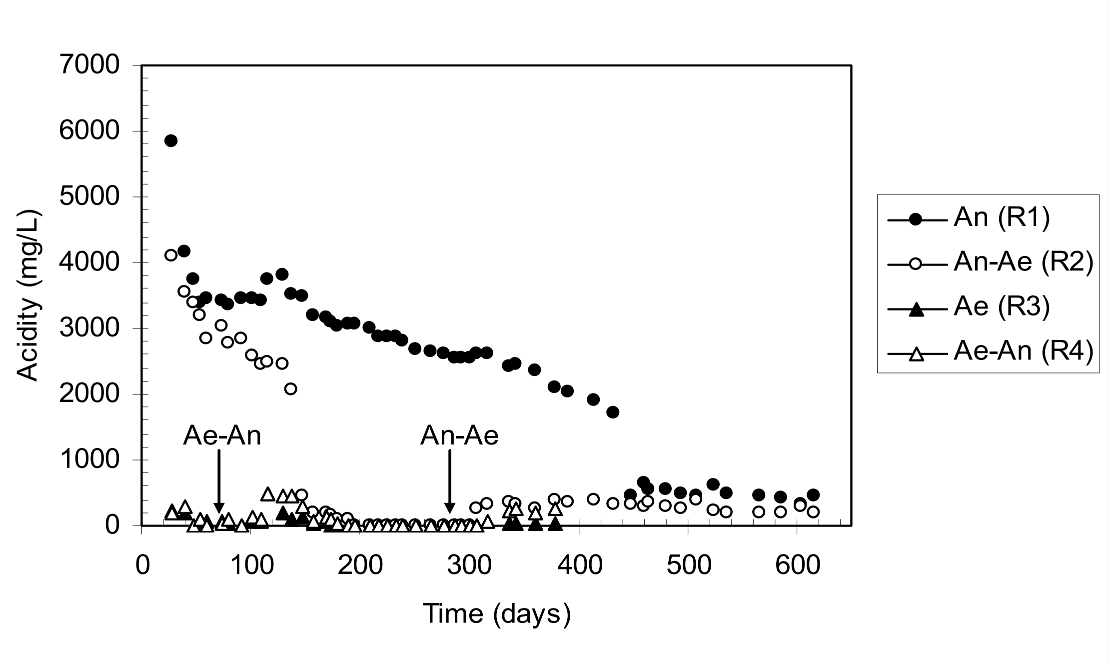

Figure 5.39. Leachate acidity concentrations

5.3.18. Sulfate and Sulfide

Sulfates and sulfides were monitored as an indicator of the presence of reducing conditions within the landfill environment. The extent to which the sulfate is reduced to sulfide is important to control the sulfide and heavy metal toxicity in anaerobic systems. In the S^{-2} form, sulfide is such a powerful precipitating agent that even at low pH values and very low sulfide concentrations, most of the sulfide generated is bound to heavy metals as metal sulfides (Pohland et al., 1987). Sulfate and sulfide concentrations for the reactors are presented in Figures 5.40 and 5.41, respectively.

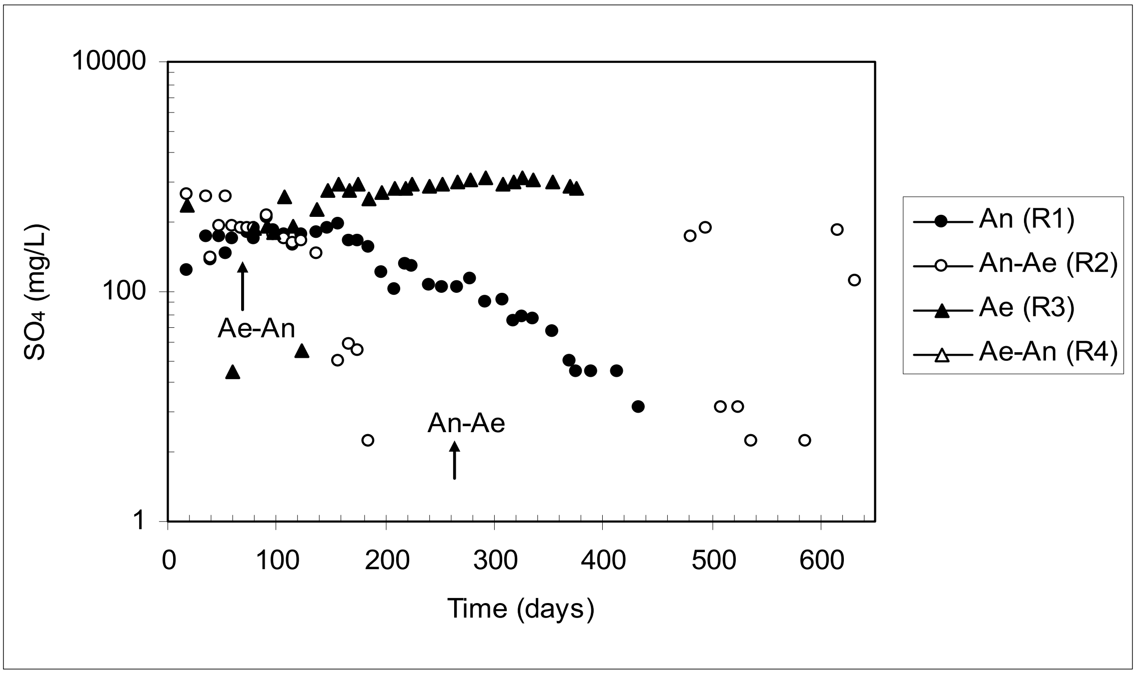

Figure 5.40. Leachate sulfate concentrations

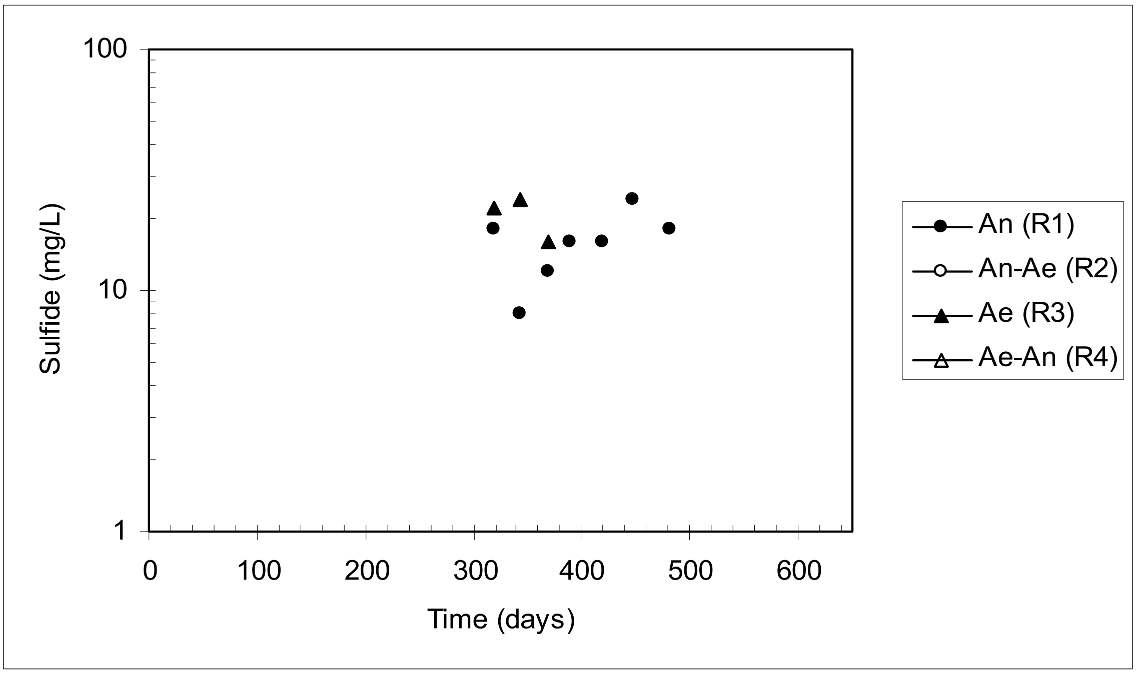

Figure 5.41. Leachate sulfide concentrations

Initial leachate sulfate concentrations of Reactors 1,2,3,4 were 150 mg/L, 700 mg/L, 575 mg/L, 0 mg/L, respectively on Day 16. In Reactor 1, together with the degradation of MSW organic fraction, the influent sulfate concentrations increased gradually at the early stages and reached the maximum value of 440 mg/L on Day 89, and then decreased to 10 mg/L on Day 431. This decrease is caused by the reduction of sulfate to sulfide as the system swiched from acidogenic to methanogenic phase. Hence sulfate in leachate can be used as an indicator of stabilization within landfills (Lens et.al., 1998). After this day, sulfate concentrations were not observed in the reactor until the end of the experiment. Sulfide concentrations were only observed between Days 316 and 480 during rapid decrease in sulfate concentrations.

In Reactor 2, high sulfate concentrations declined to zero after Day 182 due to the reduction of sulfate to sulfide and washout. Instead of air addition on Day 264, sulfate concentrations were not measured until Day 480 due to inadequate aeration. Towards the end of study, sulfate concentrations again reappeared in leachate. On the other hand, sulfide concentrations were removed rapidly from leachate by precipitation and washout mechanisms after reduction and free sulfide concentrations were not observed throughout the experiment.

At the beginning of Reactors 3 and 4, although air was added to the system, a sulfide odor was detected in the leachate, suggesting the presence of anaerobic pockets in the reactors. Since highly reducing conditions confirmed by negative ORP values were established in the reactors under aerobic conditions, sulfate concentrations were not observed except once or twice for Reactor 3. While sulfate concentrations began to appear in Reactor 3 after the onset of oxidizing conditions during Day 75, sulfate concentrations of Reactor 4 were not measured throughout the experiment due to the conversion from aerobic to anaerobic conditions. Similarly, sulfide concentrations of Reactor 4 were not observed because formed sulfides from sulfate reduction precipitated with heavy metals immediately and were not remained in the free form after precipitation. On the other hand, sulfate concentrations of Reactor 3 increased to 1000 mg/L under oxidizing conditions. Along with the presence of other ions including carbonate, phosphate, sulfate, sulfide became free and remaining sulfides were observed in the reactors as 16 mg/L at the end of experiment.

5.3.19. Chloride

Chloride was monitored as a non-biodegradable, conservative tracer in order to estimate the dilution and washout effects throughout the experiments. Chloride concentrations for all reactors are presented in Figure 5.42.

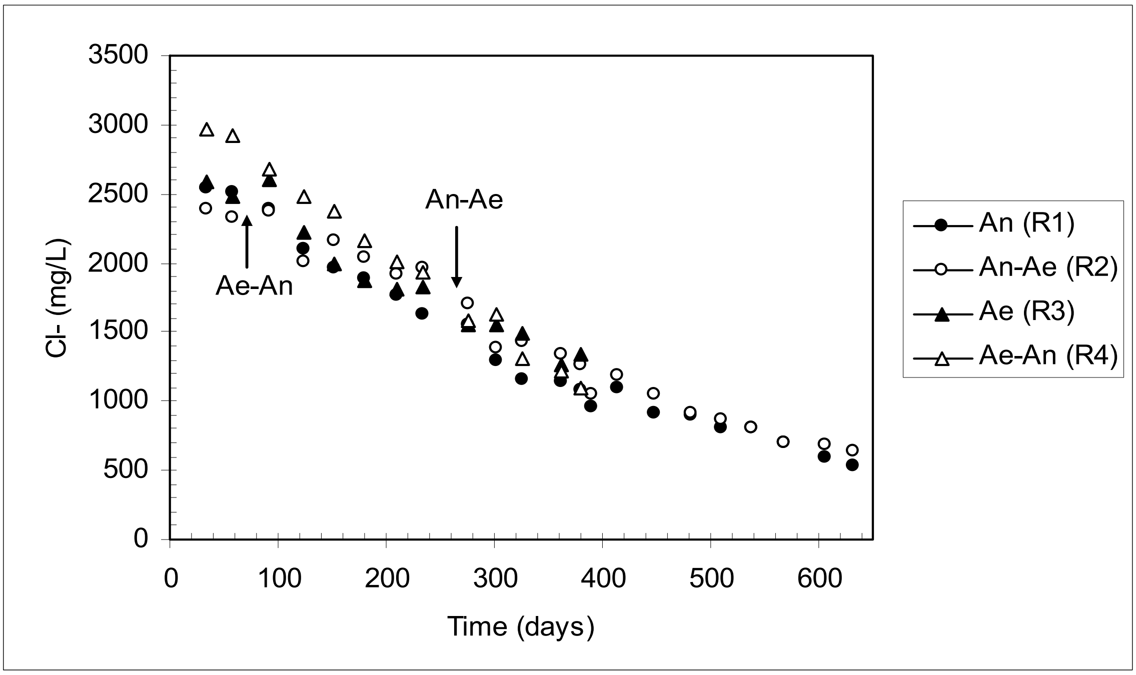

Figure 5.42. Leachate chloride concentrations

The chloride concentrations of all reactors indicated similar decreasing trend because the same amount of simulated rain water was added and same recirculation ratio was applied to the reactors. Decrease in chloride concentrations was mainly caused by the dilution effect of water used for rainfall simulation. Initial chloride concentrations were 2536 mg/L for Reactor 1, 2393 mg/L for Reactor 2, 2584 mg/L for Reactor 3 and 2968 mg/L for Reactor 4. These concentrations decreased to 538 mg/L for Reactor 1, 634 mg/L for Reactor 2 on Day 630 and 1340 mg/L for Reactor 3 and 1101 mg/L for Reactor 4 on Day 377, respectively due to the dilution effect of water and the washout.

There is a remarkably close correlation between chloride concentration and conductivity parameters. The comparison also provides a good indication regarding the reliability of both parameters. These observations have been confirmed by experimental measurements performed in the reactors.

5.3.20. Metals

Two groups of metals were anayzed during the experimental investigations: the alkali and alkaline earth metals (sodium (Na), potassium (K), Magnesium (Mg) and Calcium (Ca)) and the heavy metals (Iron (Fe), Manganese (Mn), Cadmium (Cd), Nickel (Ni), Zinc (Zn), Copper (Cu), Chromium (Cr) and Lead (Pb)).

5.3.20.1. Alkali and Alkaline Earth Metals. The alkali metals, Group 1A, include sodium and potassium. The alkaline earth metals, group 2A, include calcium and magnesium. In general, the four cations could be considered as rather conservative metals and assumed mostly affected by washout and dilution. However, the formation of organometallic complexes for calcium and magnesium, possible ion-exchange, and effects of carbonate formation should also be considered.

The change in leachate Na and K concentrations from the reactors are given in Figure 5.43 and 5.44, respectively. Both leachate Na and K concentrations from the reactors, showed the same behavior. Initial Na concentrations of Reactors 1,2,3 & 4 were 1,548 mg/L, 1,542 mg/L, 1,344 mg/L and 1,140 mg/L, respectively. Na concentrations decreased to 1,050 mg/L for Reactor 1, 456 mg/L for Reactor 2, 879 mg/L for Reactor 3 and 1,029 mg/L for Reactor 4 towards the end of study. K concentrations declined from 1,354 mg/L to 441 mg/L in Reactor 1, from 2,000 mg/L to 478 mg/L in Reactor 2, from 1,532 mg/L to 1,305 mg/L in Reactor 3 and from 2,042 mg/L to 749 mg/L in Reactor 4. Significant precipitation for Na and K has not been observed and they exist in only one oxidation state (+1) in the landfill systems (Pohland et al., 1993) and thus, their behavior was expected to be that of a conservative tracer throughout the study. Both Na and K showed evidence of dilution effects that was confirmed by chloride concentrations in the reactors. Kimmel and Braids (1980) also indicated a linear relationship between Cl^- concentrations and Na concentrations in water samples obtained in a leachate plume at different distances from a landfill.

On the other hand, Ca and Mg concentrations of the reactors indicated variation because they are more chemically complicated than Na and K, with the primary difference being that both have available and potential precipitants. Leachate calcium and magnesium concentrations depended totally on pH variations, with species such as $CaCO_3$, $Ca_{10}(PO_4)_6(OH)_2$, $CaMg(CO_3)_2$ and $Mg(OH)_2$ serving as the significant sources and sinks for these elements. In the case of calcium, the potential precipitant is carbonate ($CaCO_3$) while magnesium is subject to precipitation as the hydroxide ($Mg\ (OH)_2$). The change in leachate Ca and Mg concentrations from the reactors are given in Figure 5.44 and 5.45, respectively. Ca concentrations were measured as 3,120 mg/L for Reactor 1, 2,022 mg/L for Reactor 2, 66 mg/L for Reactor 3 and 402 mg/L for Reactor 4, at the beginning of study. The initial high Ca concentrations of Reactors 1 and 2 under anaerobic conditions decreased rapidly to 441 mg/L on Day 446 and 479 mg/L on Day 146 after the establishment of methanogenic conditions and thus with increase in pH values. On the other hand, Ca concentrations of Reactors 3 and 4 under aerobic conditions were considerably lower than Ca concentrations of Reactors 1 and 2 due to the establishment of suitable conditions for precipitation reactions previously. Ca concentrations of Reactor 3 increased slightly and stayed constant during the experiment and then reached to 109 mg/L at the end of study. In Reactor 4, Ca concentrations decreased to 98 mg/L.

Initial Mg concentrations were 340 mg/L for Reactor 1, 294 mg/L for Reactor 2, 52 mg/L for Reactor 3 and 98 mg/L for Reactor 4. In Reactors 1 and 2, Mg concentrations declined to 28 mg/L and 31 mg/L at the end of study, respectively. In Reactor 3 representing aerobic landfill, like Ca concentrations, leachate Mg concentrations increased to 143 mg/L and later decreased to 56 mg/L at the end. Similarly, final Mg concentration of Reactor 4 was 66 mg/L. As a result, Mg resembled in many ways Ca, although its affinity for ion exchange, occurrence as base saturation ion and likelihood for forming precipitates is slightly less than for Ca (Christensen et al., 2001).

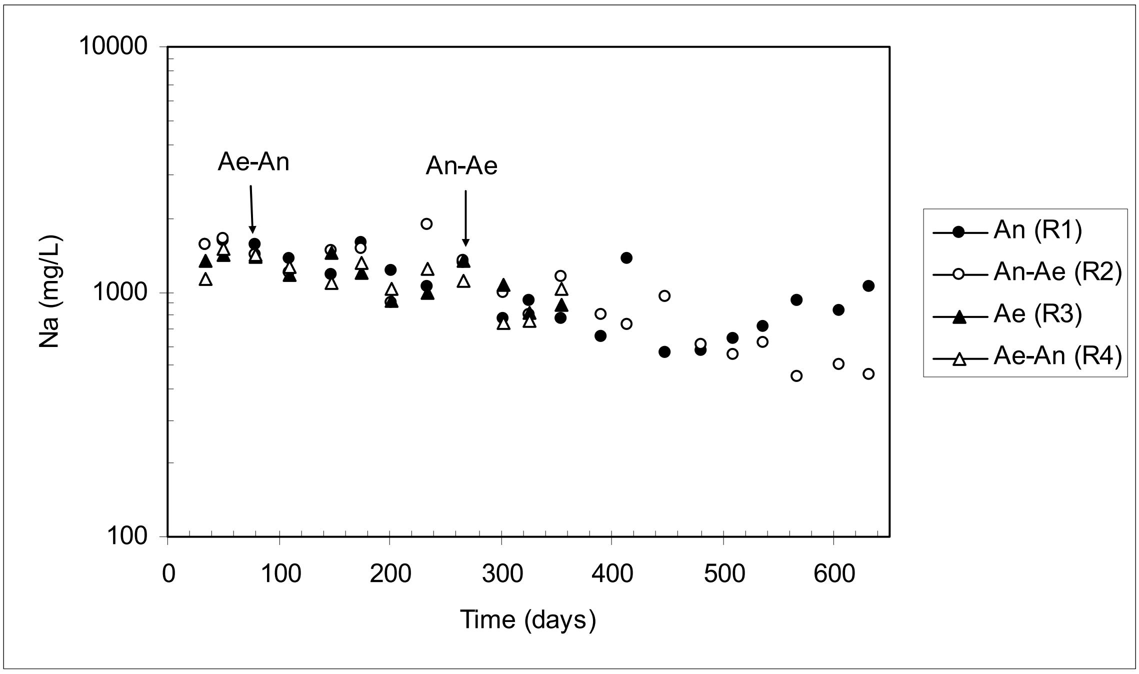

Figure 5.43. Leachate Na concentrations

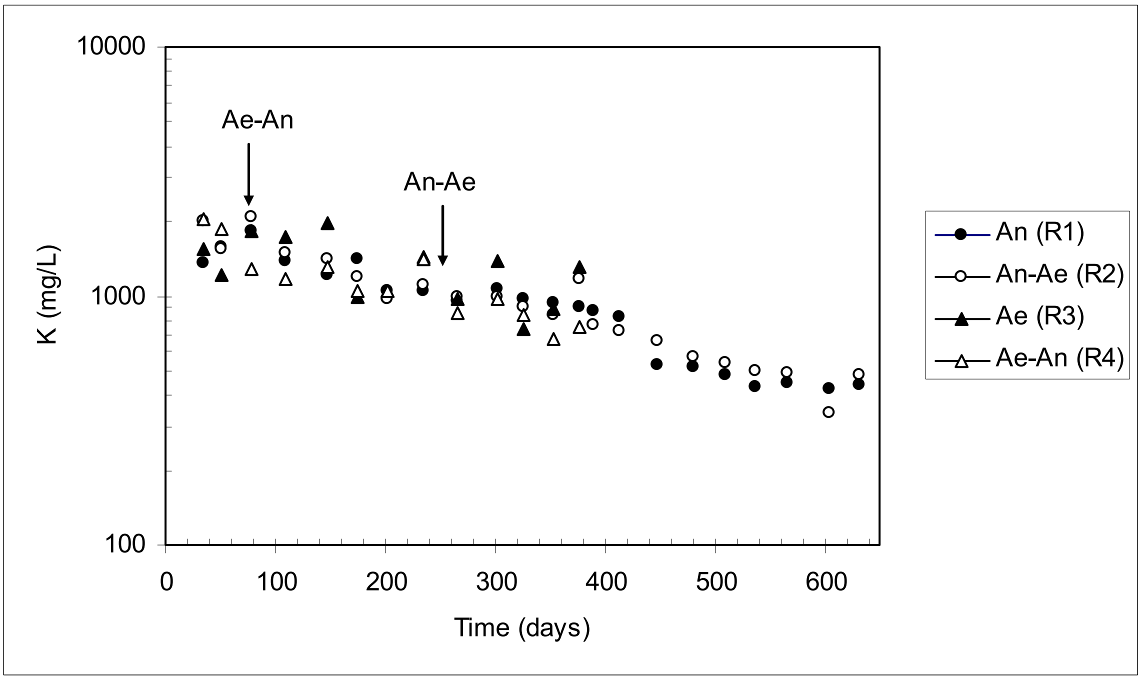

Figure 5.44. Leachate K concentrations

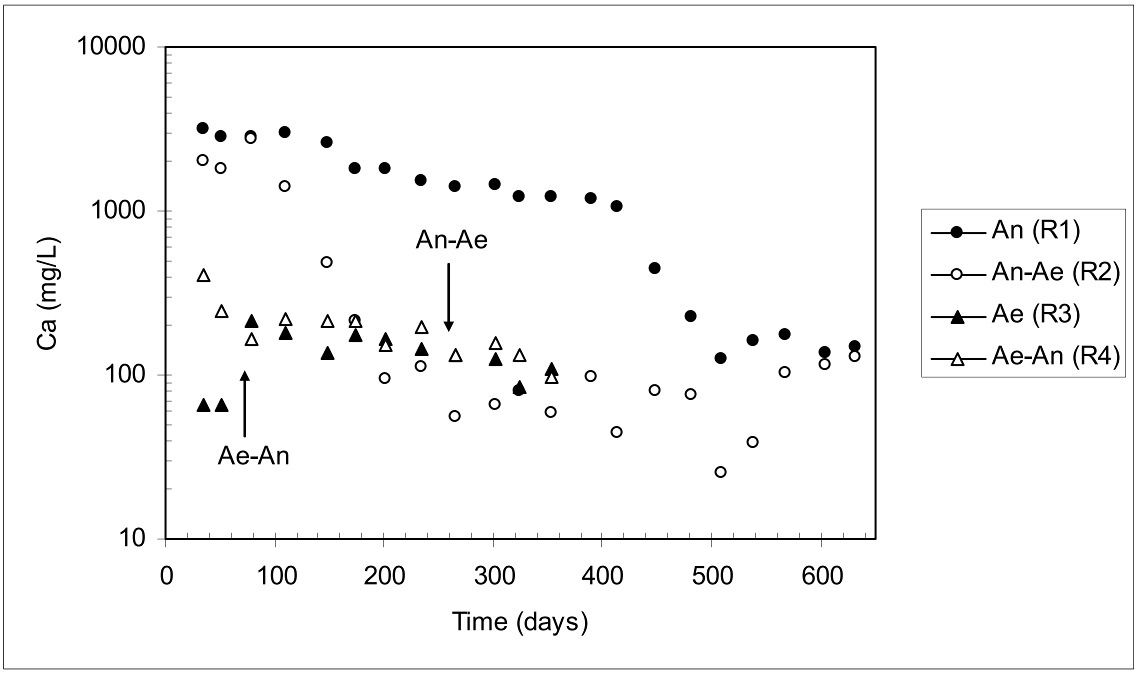

Figure 5.45. Leachate Ca concentrations

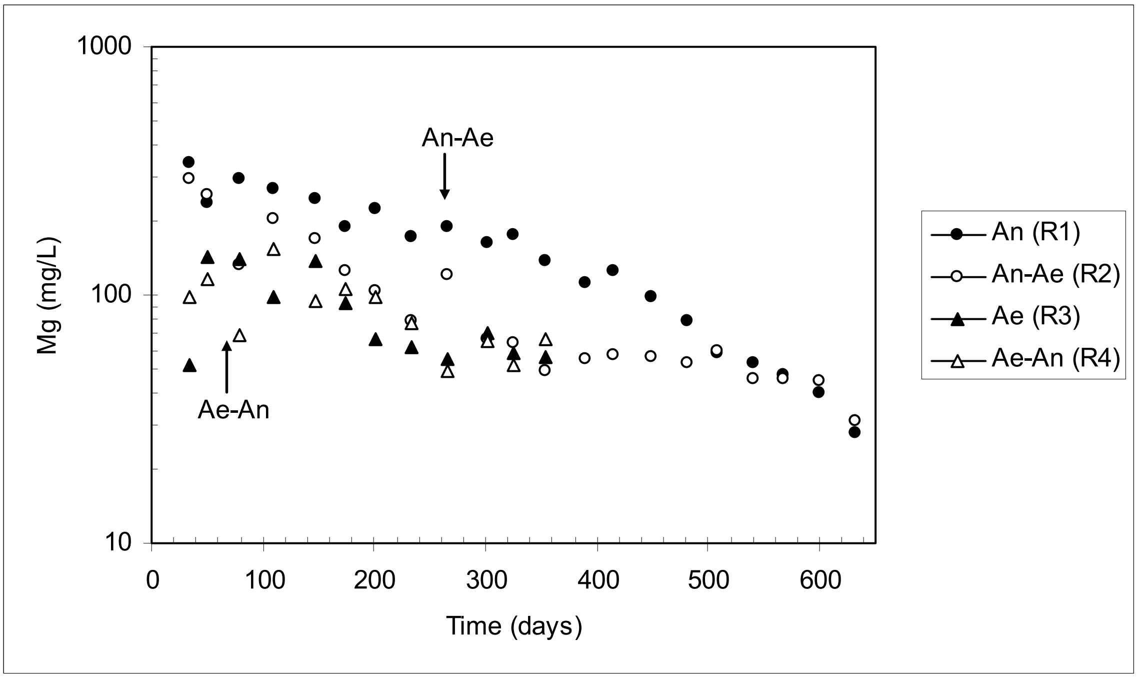

Figure 5.46. Leachate Mg concentrations

5.3.20.2. Heavy Metals. The most important factor in determining the presence of a metal in leachate is its solubility under the aerobic and anaerobic conditions prevailing within the landfill environment. Several factors influence metal solubility in leachate, including concentration of precipitant species (hydroxide, carbonate, sulfide or possibly phosphates), presence of complexing agents (ligands such as NH_3/NH_4^+, humic acids), ORP, pH, ionic strength and washout effects (Förstner et al, 1991; Benjamin, 2002).

Investigations have shown that, with the exception of Cr^{+3}, which is controlled by the solubility of its hydroxide, metal hydroxides rarely control the solubility of heavy metals in landfill leachate (Pohland et al., 1987). In addition, carbonate species have the potential for controlling the solubility of heavy metals in those circumstances where sulfide is not present. However, it is generally a modest precipitant at pH 8 or lower. Sulfide, on the other hand, is a powerful precipitant even at low pH values and very low sulfide concentrations. Because of the low solubilities of metal sulfides, sulfide can control the heavy metals with a high probability throughout the experimental studies.

Complexing agents can inverse the impact of precipitant ions and increase the solubility of metals. Usually, the complexing capabilities of inorganic ligands, carboxyls, carbohydrates and volatile acids, all recognized as present in landfill leachates, are too weak to have a substantial influence. Humic-like substances found in leachate are the one exception as they seemed to be important in the control of solubility of certain heavy metals. Moreover, oxidation-reduction potentials of leachate have a significant impact on metal speciation. Reducing conditions usually encourage conversion of Fe^{+3} to Fe^{+2} and Cr^{+6} to Cr^{+3} and would have an impact on solubility. Likewise high ionic strength increases the concentration of metals in solution by increasing the solubility over that of dilute systems.

It may be that the fate of heavy metals in aerobic systems will differ from anaerobic systems. The long term fate of heavy metals in aerated landfills is a question yet to be satisfactorily addressed.

The behavior and fate of the heavy metals in the terms of their mobility in the reactors under the aerobic and anaerobic conditions received attention in this study. The variations in the leachate concentrations of iron, manganese, nickel, zinc, copper and chromium as a function of time and pH are shown in Figures 5.47 through 5.58 .

Iron is present in aquatic systems in two oxidation states; Fe^{+3} (ferric) and Fe^{+2} (ferrous). Soluble oxidized state ferric (Fe^{+3}) and rather soluble reduced form ferrous (Fe^{+2}) irons can be transformed to each other depending upon the redox conditions. Moreover, iron may be precipitated as hydroxide or sulfide, with the hydroxide form being more important for oxidized iron (Fe^{+3}) (pK_{so}=39), and sulfide being important as a precipitant for the reduced iron (Fe^{+2}) (pK_{so}=17.2). Fe^{+3} is precipitated as a mineral deposit such as Fe_2O_3 or $Fe(OH)_3$ at a pH>5. $Fe^{+2}$is dominant in the pH range of 5 to 9 and likely to be precipitated as pyrite (FeS_2) at pH>5 under reducing conditions (Drever, 1988).

As shown in Figure 5.47, initial Fe concentrations of Reactors 1 and 2 under anaerobic conditions (95 mg/L for Reactor 1 and 120 mg/L for Reactor 2) were higher than those of Reactors 3 and 4 under aerobic conditions (2,4 and 2 mg/L, respectively). Iron concentrations of Reactor 1 increased to 152 mg/L on Day 77 and then gradually decreased. Similarly, Fe concentrations of Reactor 2 increased to its highest value of 155 mg/L on Day 49 and then decreased with increasing pH. This rise in Reactors 1 and 2 under anaerobic conditions was probably due to the dissolution of metal components during acid formation phase of the reactors. Together with rapid changes in pH of Reactor 1 on Day 446 and Reactor 2 on Day 146 to neutral conditions, Fe concentrations decreased substantially to below 10 mg/L. pH versus Fe concentration distribution for the reactors is given in Figure 5.48. There is a decreasing trend in metal concentrations of Reactors 1 and 2 as pH values rise as confirmed in the graph. In contrast to Reactors 1 and 2, initial Fe concentrations of Reactors 3 and 4 under aerobic conditions were measured below 5 mg/L on Day 32 due to the establishment of highly reducing environment and the formation of sulfide from sulfate which enabled heavy metal precipitation previously. The measurements of ORP, sulfate and conductivity confirmed the removal of the heavy metals during this period. Because Fe concentrations of Reactors 3 and 4 were scattered over the graph area for pH range 7 and 8, it is not possible to comment about relationship of acidic pH and Fe concentrations in those reactors.

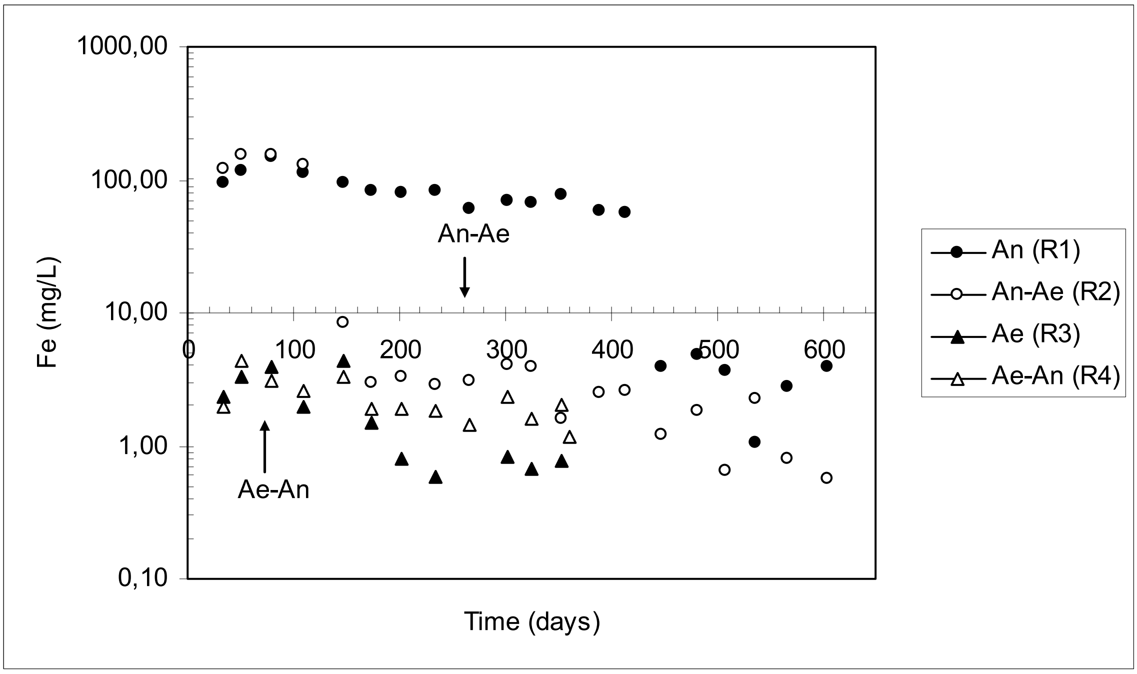

Figure 5.47. Leachate Fe concentrations

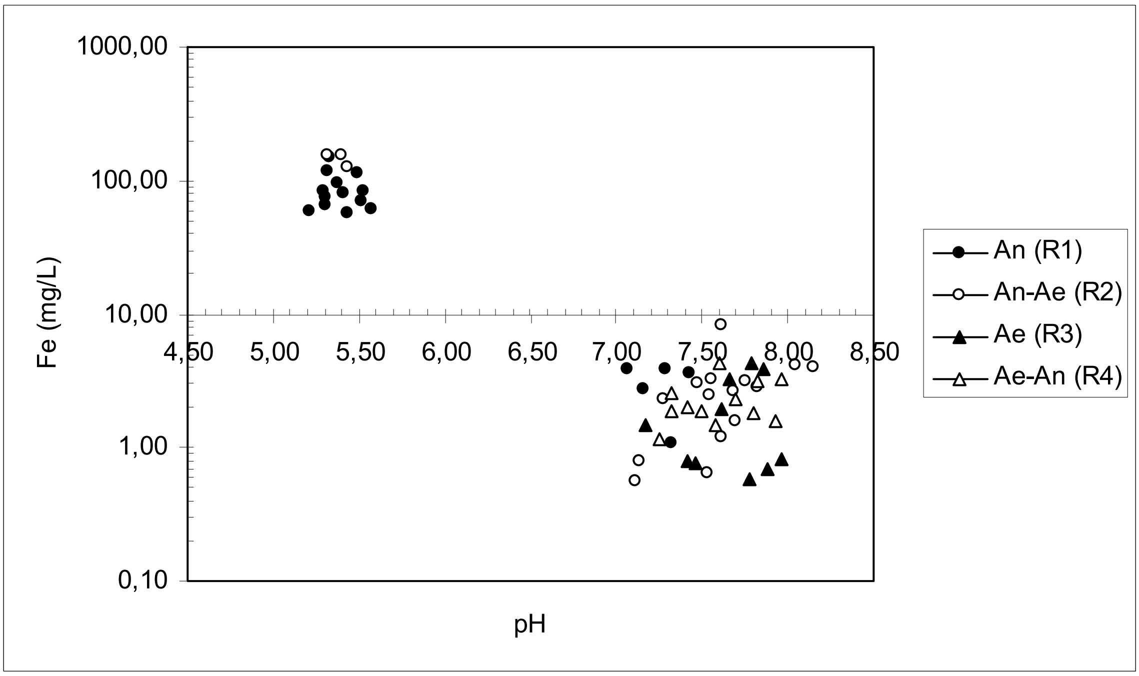

Figure 5.48. Leachate Fe concentrations vs. pH

Manganese could be expected to exist in the form of either Mn^{+2} or Mn^{+4} oxidation states. Under strongly reducing conditions, the +2 oxidation state is the dominant state. Mn^{+2} is characterized by its fairly high solubilities at pH levels below 9 and the potential for forming sparingly soluble sulfides (MnS; pK_{so}=14.0).

The change in leachate Mn from the reactors is given in Figure 5.49. The initial Mn concentrations of leachate of Reactors 1,2,3,4 were 16.91 mg/L, 11.65 mg/L, 0.198 mg/L, 0.233 mg/L respectively on Day 32. Mn concentrations in the reactors followed similar attenuation trend with Fe concentrations throughout the experimental period. Relatively high concentrations of Mn were observed for 446 days in Reactor 1 and for 146 days in Reactor 2 under anaerobic conditions. After these days, manganese concentrations decreased to below 1 mg/L due to the onset of reducing conditions in the reactors. When aerobic conditions were established in Reactor 2 on Day 264, Mn concentrations were still low inspite of slight increase. Figure 5.50 indicates that pH was neutral and suitable for immobilization of Mn concentrations in Reactor 2 during aeration period. On the other hand, Mn concentrations in Reactors 3 and 4 under aerobic conditions already were below 1 mg/L because of the establishment of highly reducing environment that was previously confirmed with low ORP values (Figure 5.3). After a slight increase, Mn concentrations declined to their lowest value. This decreasing trend was not influenced with the conversion of Reactor 4 from aerobic to anaerobic conditions. At the end of study, Mn concentrations were 0.417 mg/L for Reactor 1, 0.247 mg/L for Reactor 2, 0.03 mg/L for Reactor 3 and 0.052 mg/L for Reactor 4. Therefore, the behavior of Mn in the reactors could be explained by washout and sulfide precipitation.

Cadmium, Nickel and Zinc indicate similar attenuation mechanism. All three of these metals exist in only the +2 oxidation state, and are subject to precipitation as sparingly soluble sulfides (CdS, $pK_{so} = 26.1$; NiS, $pK_{so} = 24.0$; ZnS, $pK_{so} = 23.8$). None of these metals is subject to significant complexation with any of the important inorganic ligands in leachates. Once active sulfate reduction/ sulfide generation commenced, these elements could be expected to be removed by precipitation as the respective sulfides and physical entrapment in the waste matrix.

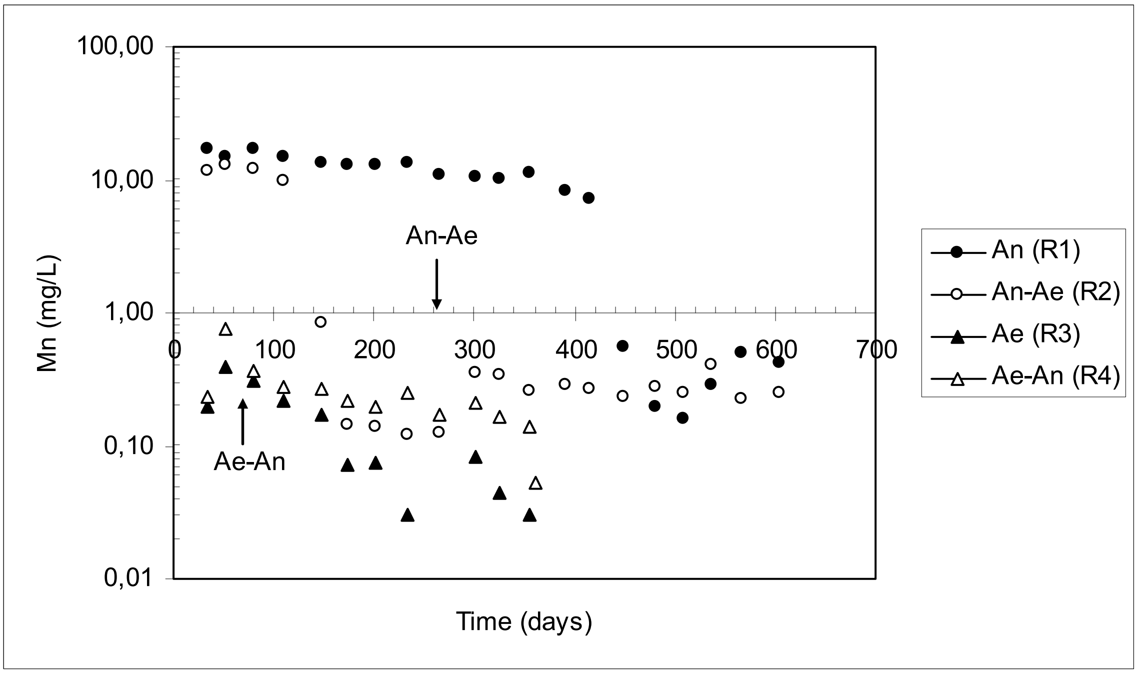

Figure 5.49. Leachate Mn concentrations

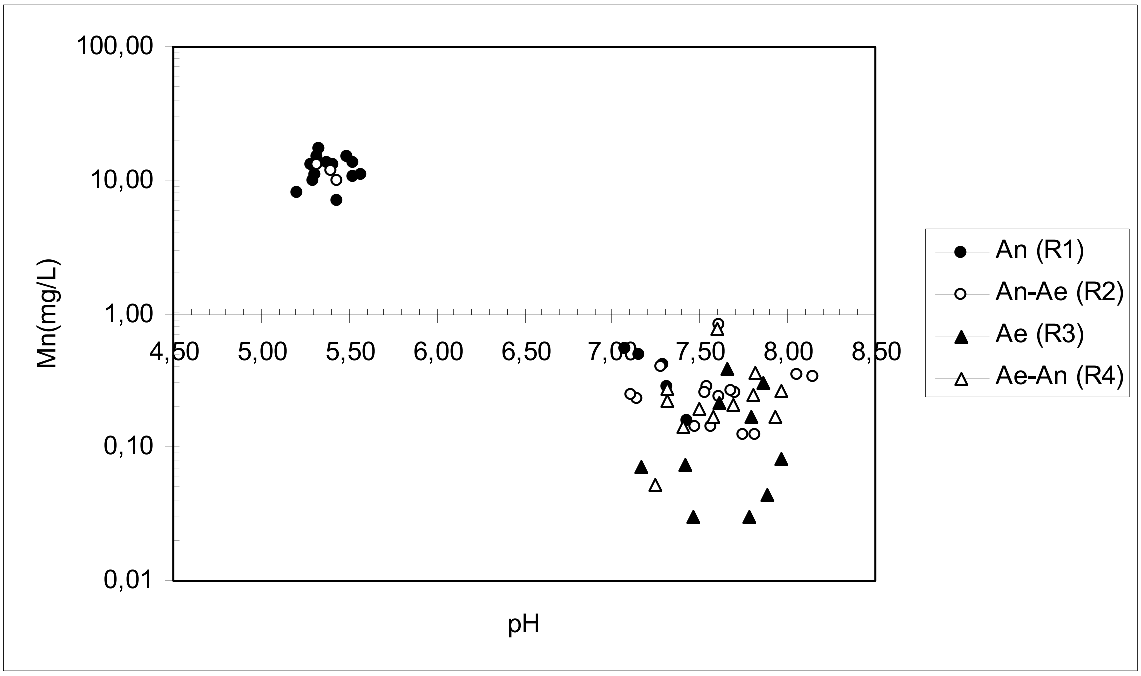

Figure 5.50. Leachate Mn concentrations vs. pH

Cadmium concentrations was not detected in leachate from all reactors. The change in leachate Ni and Zn concentrations from the reactors are given in Figure 5.51 and 5.53, respectively. The initial Ni and Zn concentrations of the reactors were lower than Fe and Mn concentrations. The initial leachate Ni concentrations of Reactors 1,2,3,4 were 0.584 mg/L, 0.395 mg/L, 0.032 mg/L, 0.017 mg/L respectively on Day 32. The initial leachate Zn concentrations of Reactors 1,2,3,4 were 0.794 mg/L, 0.497 mg/L, 0.067 mg/L, 0.043 mg/L respectively on Day 32. Maximum Ni and Zn concentrations were determined as 0.587 mg/L and 1.068 mg/L in Reactor 1 and 0.407 mg/L and 0.633 mg/L in Reactor 2, respectively. While Ni concentrations of Reactors 1 and 2 decreased below 0.1 mg/L after 500 days of operation, Zn concentrations declined below 0.1 mg/L on Day 412 for Reactor 1 and on Day 200 for Reactor 2. pH versus Ni and Zn concentration distributions indicate that the lowest Ni and Zn concentrations of Reactors 1 and 2 were observed in the pH range of 7.0 and 7.4 (Figure 5.52 and 5.54). On the other hand, Ni and Zn concentrations of Reactors 3 and 4 under aerobic conditions were less than Reactors 1 and 2 throughout the experiment. Especially, Ni concentrations of Reactors 3 and 4 under aerobic conditions were very low for about first 100 days when compared to the other days due to the establishment of highly reducing environment and the formation of sulfide from sulfate which was providing heavy metal precipitation until this day and remained below 0.1 mg/L until last day of the experiment. The measurements of ORP, sulfate and conductivity confirmed the removal of the heavy metals during this period. Zn concentrations of Reactors 3 and 4 also indicated same behavior and measured as 0.074 mg/L and 0.105 mg/L, respectively at the end of the study. Final Zn concentrations of these reactors were observed as higher than their initial concentrations. However,it should be noted that observed Zn concentrations (below 0.5 mg/l) are far below the Turkish Water Pollution Control Regulation discharge limit of 5.0 mg/l.

Copper occurs in metallic form or in compounds as Cu^{+} or Cu^{+2} (Scheinberg, 1991). The predominant copper species occur as the divalent cation Cu^{+2} up to pH 6 (Ünlü, 1998). Copper solubility is controlled by OH^{-}, Fe and/or sulfide as chalcocite (Cu_2S), chalcopyrite ($CuFeS_2$), cuprite (Cu_2O) and malachite ($Cu_2(OH)_2CO_3$). In the case of copper, the potential precipitant is sulfide (CuS, $pK_{so} = 44.1$; Cu_2S, $pK_{so} = 46.7$). Sulfide at pH 8.5 will result in effluent copper concentrations of 0.01 to 0.02 mg/L (Eckenfelder, 1989).

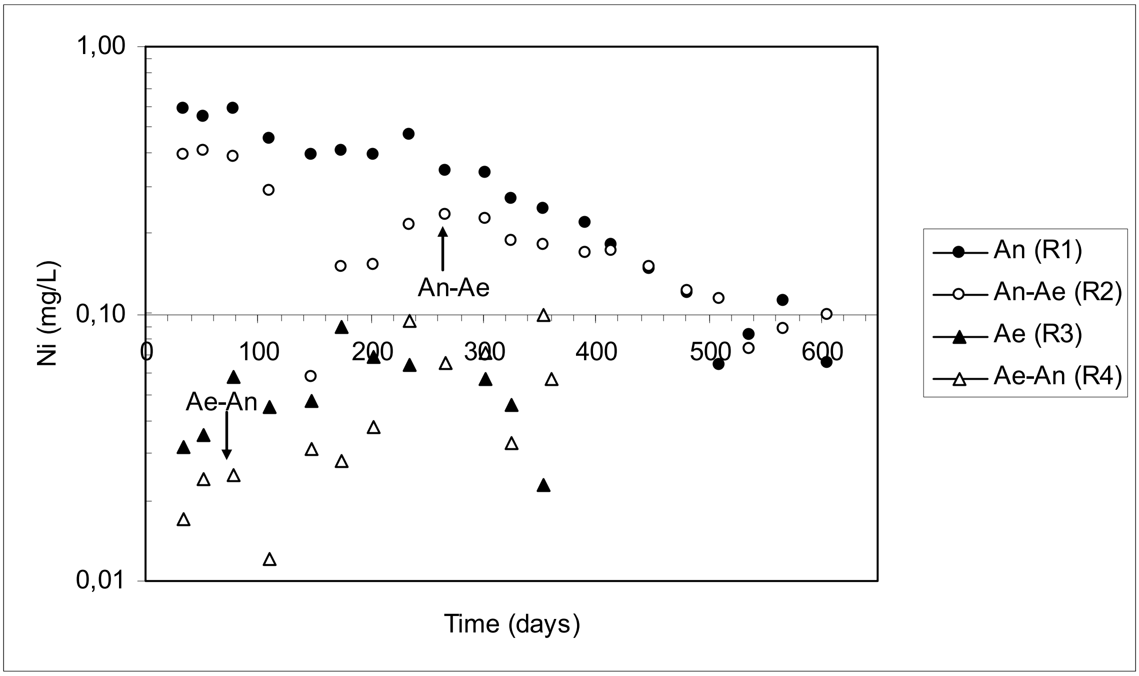

Figure 5.51. Leachate Ni concentrations

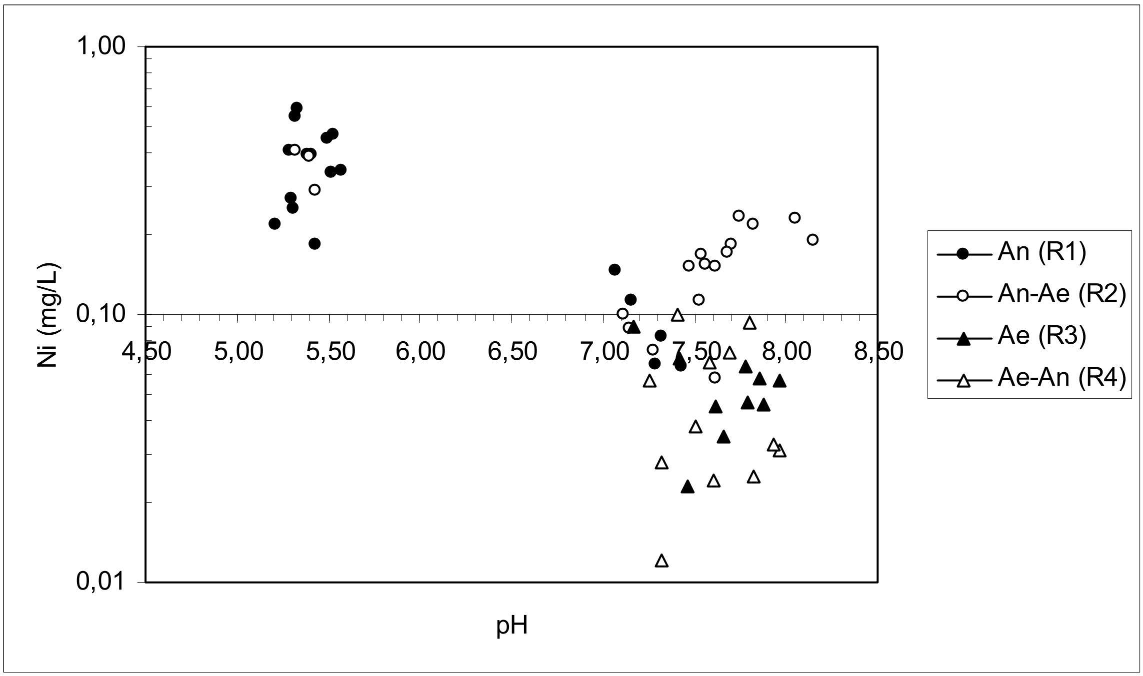

Figure 5.52. Leachate Ni concentrations vs. pH

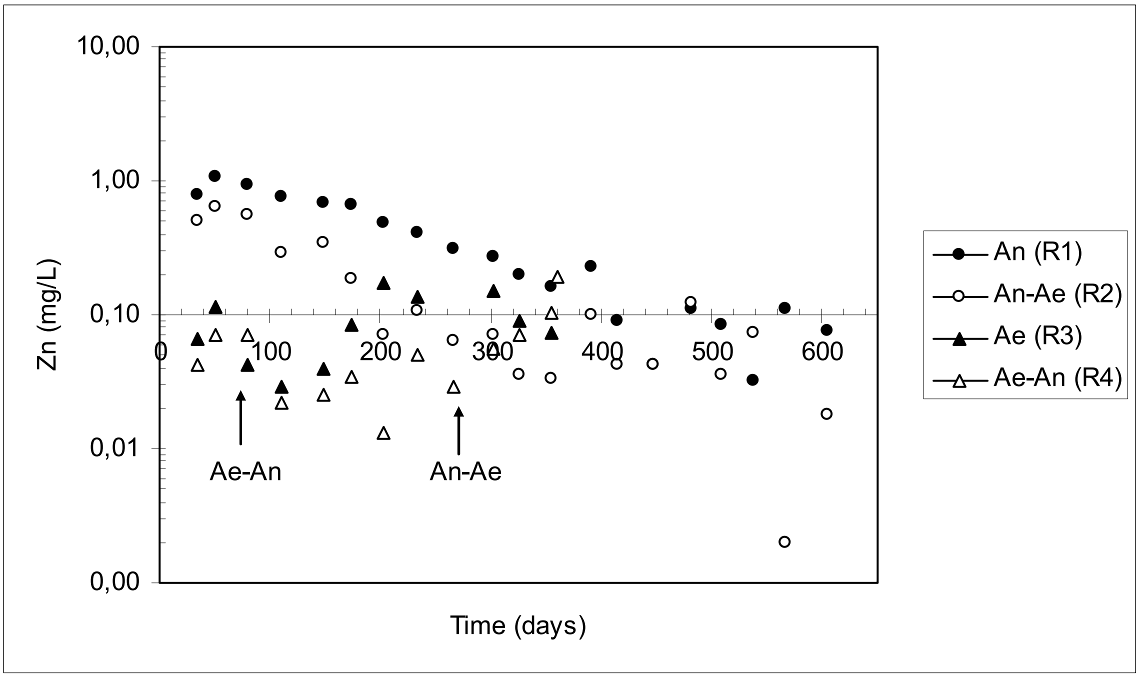

Figure 5.53. Leachate Zn concentrations

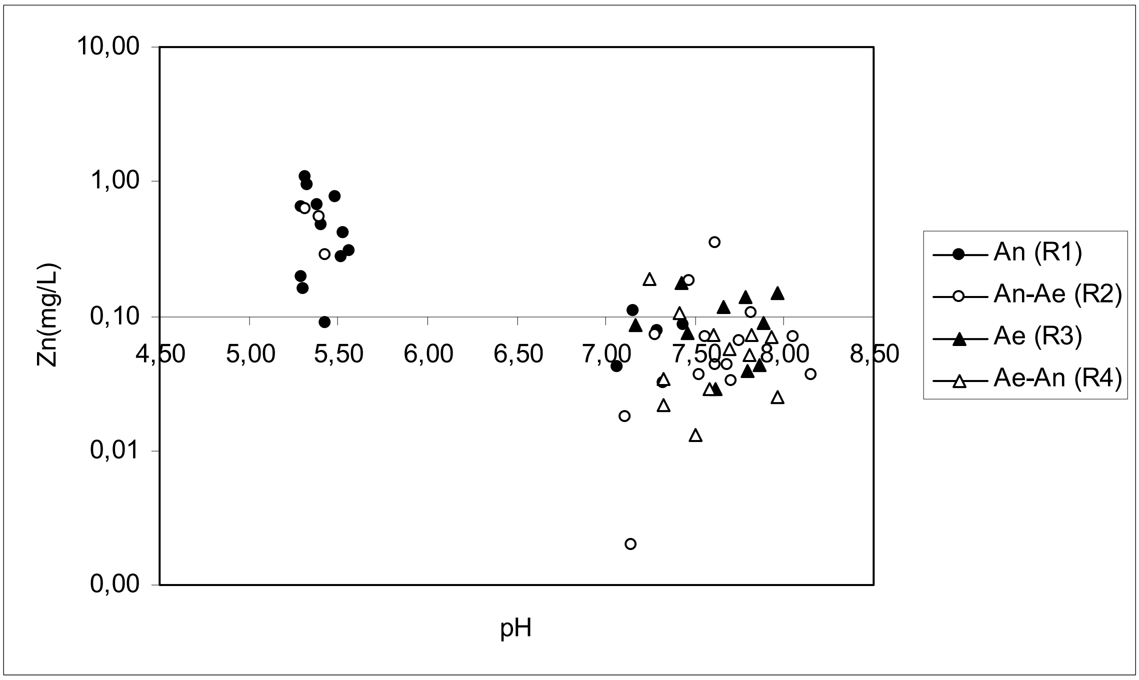

Figure 5.54. Leachate Zn concentrations vs. pH

The change in leachate Cu concentrations from the reactors are given in Figure 5.55. At the beginning of the experiment, Cu concentrations were determined below 0.1 mg/L in all reactors. Initial Cu concentrations of Reactors 1, 2, 3 &4 were 0.045 mg/L, 0.055 mg/L, 0.055 mg/L and 0.051 mg/L. In Reactors 1 and 2, Cu concentrations increased to higher concentrations after the onset methanogenic conditions together with rapid shifting of pH from acidic to neutral values. Christensen et al., 2001 explained that for Cd, Ni and Zn, the overall migration velocity decrases with increasing pH. For copper, the consequences are reversed. Complexation of Cu increases very dramatically with pH, leading to the highest overall migration velocities for Cu at high pH values. pH versus Cu concentration distributions indicate that the lowest Cu concentrations of Reactor 1 were observed in the pH range of 5.2 and 5.6 (Figure 5.56). Final Cu concentrations of Reactors 1 and 2 were 0.05 mg/L and 0.03 mg/L, respectively.

Initially, Cu concentrations in Reactors 3 and 4 followed similar change because the reactors were operated under the same conditions until day 77. However, while copper concentrations of Reactor 4 were slightly decreasing after the conversion from aerobic to anaerobic, copper concentrations of Reactor 3 representing aerobic landfill increased visibly higher concentrations than other reactors. Copper concentration of this reactor increased to 0.18 mg/L at the end of experiment. This could be due to enhanced leaching under aerobic conditions. Complexation of Cu increases very dramatically with alkali and oxidizing conditions, leading to the highest overall migration for Cu at high pH values. Kim (2005) and Inanç et al., (2007) indicated that aerobic landfills have greater Cu leaching potential due to the oxidation. Another possibility of copper leaching from the aerobic reactor is the binding of Cu with ammonium (NH_4^+) (Figure 5.35). Since both Cu and ammonium are cations, their complexations are present as an ionic form and can be dissolved in aquatic systems (Kim, 2005). However, it should be noted that observed copper concentrations (below 0.5 mg/l) are also far below the Turkish Water Pollution Control Regulation discharge limit of 3.0 mg/l.

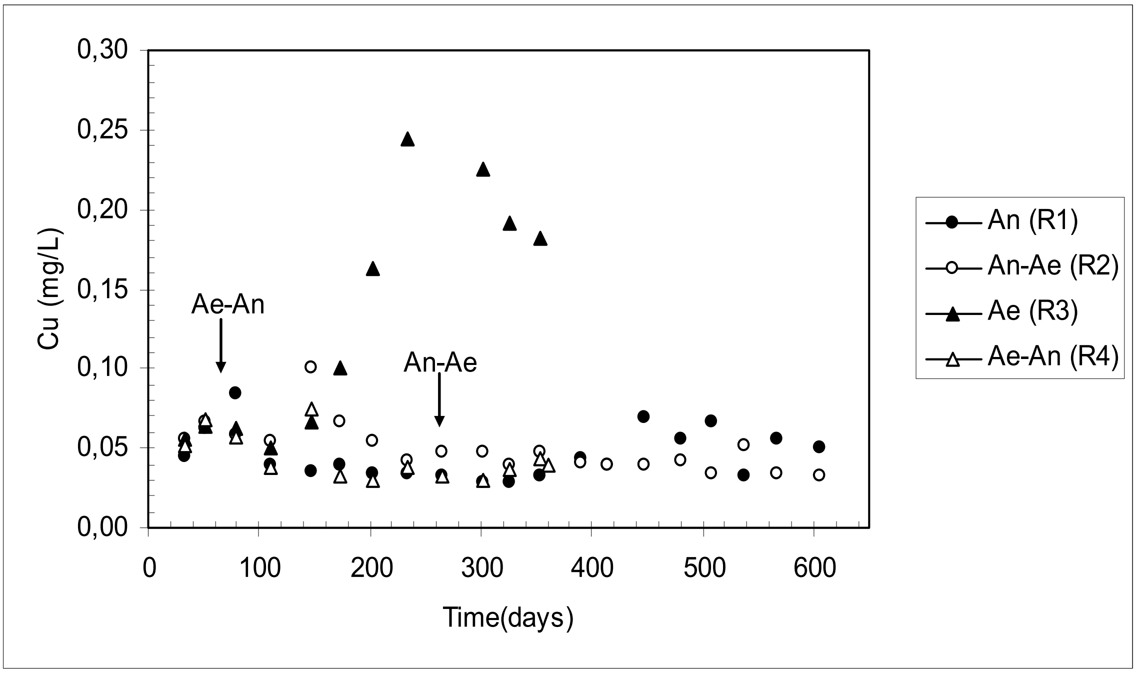

Figure 5.55. Leachate Cu concentrations

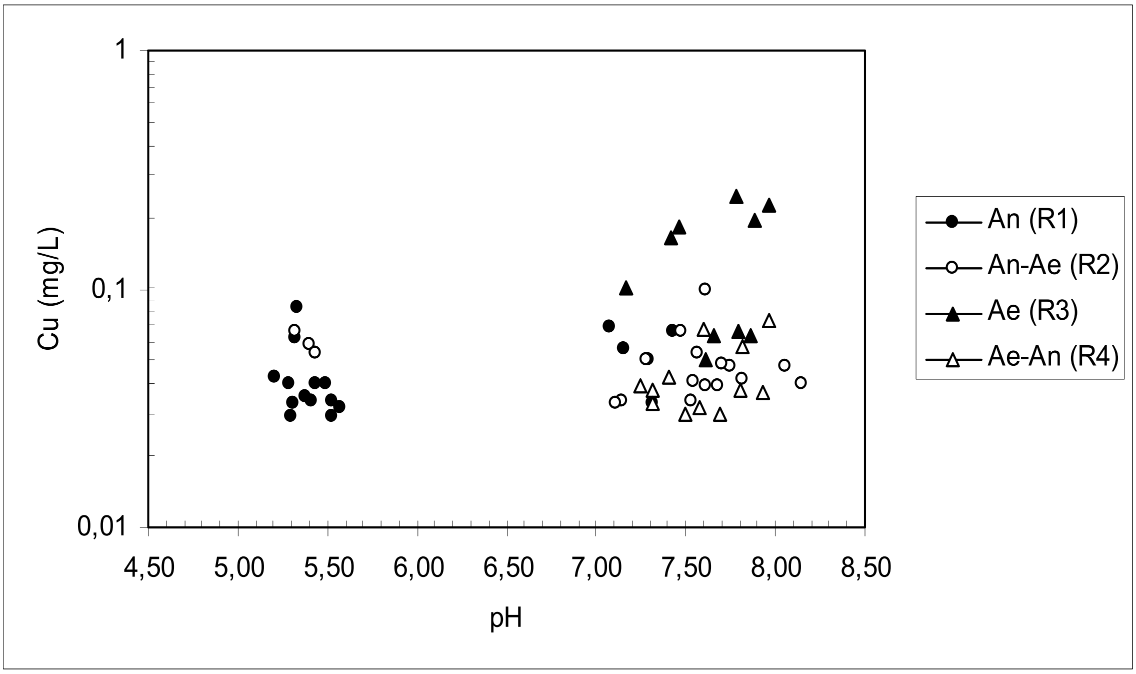

Figure 5.56. Leachate Cu concentrations vs. pH

Chromium (Cr) exists in two possible oxidation states in leachate: the trivalent chromium, Cr^{+3} and the hexavalent chromium, Cr^{+6}. The toxicity of Cr is determined by its oxidation state. Hexavalent Cr is considered more toxic than trivalent Cr due to its high mobility and solubility. Cr^{+6} becomes unstable and may be reduced to Cr^{+3} at low ORP and pH values. In order to maintain the oxidation state of Cr as Cr^{+6} at a low pH, it is necessary to keep highly oxidizing conditions (Richard and Bourg, 1991). In contrast to other metals such as Fe, Zn,Ni, Cu, and Cd, Cr^{+3} is not likely to precipitate with sulfide. Chromium solubility is mainly controlled by $Cr(OH)_3$. Generally, $Cr(OH)_3$ is formed in a pH range of 6.5 to 7 under moderately oxidizing or reducing conditions.

The change in leachate Chromium (Cr) concentrations from the reactors is given in Figure 5.57. pH versus Cr concentrations from the reactors is indicated in Figure 5.58. Initial Cr concentrations of Reactors 1, 2, 3 &4 were 0.069 mg/L, 0.098 mg/L, 0.043 mg/L and 0.099 mg/L. Final Cr concentrations of the Reactor 1, 2, 3 &4 were 0.036 mg/L, 0.031 mg/L, 0.018 mg/L and 0.037 mg/L, respectively at the end of experiment. Cr concentrations were highly scattered throghout the experiment but still they were quite below the discharge limits for all reactors. Polettini and Pomi (2003) has observed higher Cr leaching from bottom ash samples treated with air, and commented that it would be due to higher solubility of oxidized chromium forms. However in this research, total Cr concentrations were observed the lowest values for aerobic reactor when compared to other reactors. Although total amounts of Cr leached were not considerably high, it is necessary to pay great attention to hexavalent chromium (Cr^{+6}) that is highly toxic metal causing decreased pulmonary function and pneumonia (Bradle, 2005). Among Cr species dissolved in leachate, Cr^{+3} can be dominant in current anaerobic sanitary landfills, however, thermodynamically Cr^{+6} becomes a major Cr component in the environment formed on air instrusion. It is not possible to make a conclusion on our observations since we did not quantify the oxidized and reduced forms of chromium in this study.

The chemistry of lead is complicated by the array of available chemical interactions. Most Pb concentrations in alkali conditions may be precipitated as forms of PbCO3 or PbS depending on redox potentials. However, Pb concentrations were not detected for leachate from all reactors.

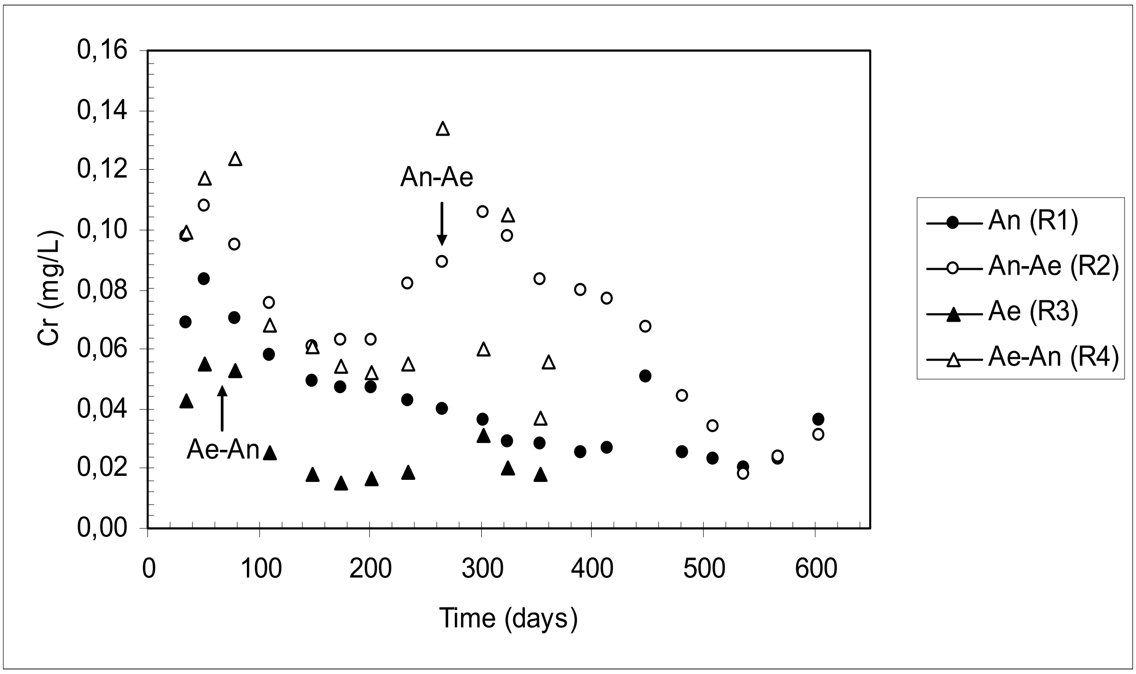

Figure 5.57. Leachate Cr concentrations

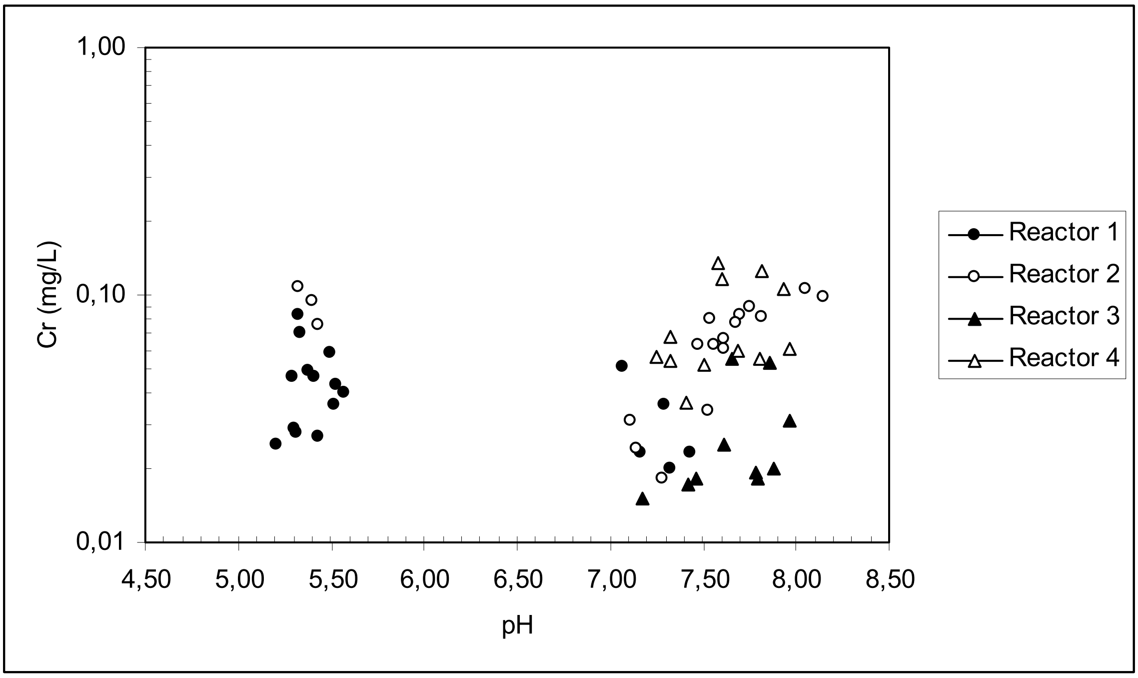

Figure 5.58. Leachate Cr concentrations vs. pH

There are numerous studies in which researchers have reported metal concentrations from full-scale landfills, test cells and laboratory studies under anaerobic conditions (Yenigun et al., 1996; Flyhammar et al., 1998; Kruempelbeck and Ehrig, 1999; Revans et al., 1999; Erses and Onay, 2003). The release of metal into leachate is generally low in anaerobic landfills in spite of acidogenesis. This is because metals tend to form hydroxides or undergo sulfidation in the anaerobic phase and the majority of these compounds are not readily soluble (Rich et al.,2007). Once aerobic conditions are re-established in the final aerobic phase metals are still immobile.

On the other hand, few studies are available in the literature reporting the leaching behavior of heavy metals from aerobic landfill bioreactors. Hantsch et al. (2003) have reported no noticeable increase in heavy metal concentration in the leachates of aerobic lysimeters compared to anaerobic lysimeters which were filled with excavated waste from an old landfill. Ritkowski and Stegmann (2003) have observed increases in Ni, Cu and Cd with no noticeable change in Cr leaching at ORP values between +200 and 250mV created by aeration of lysimeters. However, concerning the leachability of total content, only 0.02–0.5% of the heavy metals were mobilized into leachate. Since, the leachability was correlated with ORP values, they recommended aeration rates low enough not to increase ORP values significantly. In another study, heavy metal leaching from aerobic and anaerobic landfill bioreactor test cells for co-disposed municipal solid waste incineration (MSWI) bottom ash and shredded low-organic residues has been investigated by İnanc et.al. Aerobic, anaerobic and control test cells were operated for 1 year. Heavy metals which were comparatively higher in leachate of aerobic cell were copper (Cu), lead (Pb), boron (B), zinc (Zn), manganese (Mn) and iron (Fe), and those apparently lower were aluminum (Al), arsenic (As), molybdenum (Mo), and vanadium (V). However, no significant release of heavy metals under aerobic conditions was observed compared to anaerobic and control cells.

Table 5.6 shows the range of the leachate heavy metal concentrations from the reactors under aerobic and anaerobic conditons depending on pH. Slightly higher metals concentrations were stated only in leachate from the reactors under anaerobic conditions (during the acidification stage) because of high degree of metal solubilization as a result of low pH caused by production of organic acids. As the reactor age increased, further increase in pH values caused a certain decrease in metal solubility. This results in a drastic fall of the metal concentrations.

Table 5.6. The range of heavy metal concentration in the reactors

		Aerobic Conditions		Anaerobic Conditions	
		pH < 7 (acidic)	pH>7 (alkaline)	pH < 7 (acidic)	pH> 7 (alkaline)
Reactor 1	Fe (mg/L)			151.50-56.79	**4.75-1.06**
	Mn (mg/L)			16.95-7.13	0.55-0.16
	Ni (mg/L)			0.59-0.18	0.15-0.06
	Zn (mg/L)			**1.07-0.09**	**0.11-0.04**
	Cu (mg/L)			**0.08-0.03**	**0.07-0.03**
	Cr (mg/L)			**0.08-0.03**	**0.05-0.02**
Reactor 2	Fe (mg/L)		**4.10-0.56**	155.40-120.30	**8.35-2.83**
	Mn (mg/L)		0.40-0.12	12.97-9.75	0.84-0.12
	Ni (mg/L)		0.23-0.08	0.41-0.29	0.23-0.06
	Zn (mg/L)		**0.12-0.002**	**0.63-0.29**	**0.35-0.07**
	Cu (mg/L)		**0.05-0.03**	**0.07-0.05**	**0.1-0.04**
	Cr (mg/L)		**0.1-0.02**	**0.11-0.08**	**0.09-0.06**
Reactor 3	Fe (mg/L)	-	**4.36-0.58**		
	Mn (mg/L)	-	0,39-0.03		
	Ni (mg/L)	-	0.09-0.02		
	Zn (mg/L)	-	**0.18-0.03**		
	Cu (mg/L)	-	**0.25-0.05**		
	Cr (mg/L)	-	**0.06-0.02**		
Reactor 4	Fe (mg/L)	-	**4.35-2.00**		**3.26-1.16**
	Mn (mg/L)	-	0.76-0.23		0.36-0.14
	Ni (mg/L)	-	0.03-0.02		0.1-0.01
	Zn (mg/L)	-	**0.07-0.04**		**0.1-0.02**
	Cu (mg/L)	-	**0.07-0.05**		**0.07-0.03**
	Cr (mg/L)	-	**0.11-0.10**		**0.13-0.04**

On the other hand, in the reactors under aerobic conditions, the range of metal concentrations were fairly low (Table. 5.6). The discharge limits to receiving environment from landfills determined by Water Contamination Control Regulation of Turkish Government is given in Table 5.7. Heavy metal concentrations in aerobic landfill leachate samples are below the regulation limits in all periods of degradation. Zn, Cu and Cr concentrations are below the limits in anaerobic landfill reactors. There is no limit for Mn and Ni concentrations in the regulation. Besides, the values are in agreement with the literature data. For example, a review of 106 Danish landfills showed that metal concentrations for all landfills were low – 0.006 mg Cd/L, 0.13 mg Ni/L, 0.67 mg Zn/L, 0.07 mg Cu/L, 0.07 mg Pb/L and 0.08 mg Cr/L (Christensen et al., 2001),

Table 5.7. Limits for metals in Turkish water pollution control regulation

Parameter	Discharge Limit
Total Chromium (Cr)	2
Chromium(Cr^{+6})	0.5
Lead (Pb)	2
Cadmium (Cd)	0.1
Iron (Fe)	10
Copper (Cu)	3
Zinc (Zn)	5

Based on metal results, the metal leaching behavior of the reactors can be predicated. The complex chemical and physical environment of the bioreactors, as confirmed by the observed leachate properties and other characteristics, mediated the behavior of indigenous heavy metals. Leachates were rich in an array of inorganic anions. For example, chloride which was present in all reactors at levels well in excess of 2,000 mg/L at the beginning of study acted as reasonably conservative tracers and showed clear evidence of washout (Figure 5.42). Sulfate reduction with consequent formation and release of sulfide began to a significant degree coincidentally with the onset of methanogenesis (Figure 5.40). In addition carbon dioxide production provided a potential source of bicarbonate and carbonate anions once the acid formation was completed during aerobic and anaerobic degradation and leachate pH levels increased (Figure 5.2). Orthophosphate were detected at levels which could impact on metal behavior during this project (Figure 5.37)

The other significant inorganic cation in addition to the metals and hydrogen ion present during the study was the ammonium ion (NH_4^+) (Figure 5.35). In terms of potential reactivity with the heavy metals, this cation is largely nonreactive. If the pH had risen high enough to permit significant dissociation of ammonium to form ammonia (pKa=9.3), some complexation might have occured, especially with Cd, Ni, Zn and Fe. Leachate pH levels were typical acidic during the acid formation phase initially, and then increased to levels somewhat in excess of neutrality following the onset of methanogenesis. ORP values throughout the experiments were sufficiently reducing (Figure 5.3) to permit the reduction of sulfate to sulfide with eventual complete depletion of leachate sulfate in the reactors.

The reactors were also characterized by high concentrations of organic carbon (Figure 5.21). The nature of this organic matter was necessarily complex; arising as it did from both washout of soluble materials from the refuse mass and from products of chemical and biological conversion. Volatile acids decrease pH values and correspond significant heavy metals concentration in the reactors. Furthermore, humic-like substances have been associated with significant heavy metal complexation capabilities. However, this suspected remobilization could not be confirmed because humic-like organics were not measured.

Furthermore, heavy metal analysis results were evaluated by SPSS 15.0 program to understand the effects of these paramater on the behavior and fate of heavy metals. Pearson correlation analysis was subsequently performed to indicate the possible relationships between the heavy metals and analyzed parameters of Reactors (Table 5.8). Values in the table (Pearson correlation coefficient) are shown that the degree of relationship between two variables. In this study, good correlations between parameters were evaluated according to Table 5.9 suggested by Cohen (1988). Moreover, correlation results are statistically significant when significance coefficient is smaller than 0.05.

Table 5.8. Pearson’s statistical analysis of heavy metals from the reactors

Reactors	**Heavy Metals**	**TOC**	**SO_4^{2-}**	**ORP**	**pH**	**NH_3**	**Cl^-**	**PO_4^{3-}**	**CO_3^{2-}**
Reactor 1	Fe	**,935(**)**	**,825(**)**	**,639(**)**	**-,870(**)**	-,158	**,897(**)**	**,791(**)**	**,819(**)**
	Mn	**,955(**)**	**,828(**)**	**,715(**)**	**-,916(**)**	-,133	**,900(**)**	**,783(**)**	**,848(**)**
	Ni	**,906(**)**	**,861(**)**	**,588(**)**	**-,780(**)**	-,157	**,963(**)**	**,869(**)**	**,892(**)**
	Zn	**,790(**)**	**,907(**)**	,436	**-,623(**)**	-,231	**,966(**)**	**,920(**)**	**,792(**)**
	Cu	-,231	,009	**-,681(**)**	,370	-,277	,072	,211	-,098
	Cr	**,672(**)**	**,768(**)**	,228	**-,466(*)**	-,303	**,888(**)**	**,876(**)**	**,675(**)**
Reactor 2	Fe	**,974(**)**	**,862(**)**	**,503(*)**	**-,953(**)**	-,007	**,671(**)**	**,947(**)**	,221
	Mn	**,964(**)**	**,897(**)**	**,491(*)**	**-,959(**)**	-,046	**,666(**)**	**,974(**)**	,200
	Ni	**,785(**)**	**,790(**)**	**,524(*)**	**-,748(**)**	,275	**,710(**)**	**,852(**)**	**,488(*)**
	Zn	**,923(**)**	**,842(**)**	**,623(**)**	**-,838(**)**	,043	**,787(**)**	**,896(**)**	,330
	Cu	**,492(*)**	,249	**,630(**)**	-,266	,290	**,695(**)**	,318	**,452(*)**
	Cr	,439	,385	**,638(**)**	-,235	**,650(**)**	**,668(**)**	**,458(*)**	**,744(**)**
Reactor 3	Fe	,181	**-,718(*)**	-,254	,000	**,652(*)**	**,704(*)**	,256	**,635(*)**
	Mn	,265	**-,874(**)**	-,514	,077	**,882(**)**	**,858(**)**	,535	**,827(**)**
	Ni	-,362	,402	,470	-,088	-,440	-,084	-,381	-,275
	Zn	,477	**-,947(**)**	**-,646(*)**	-,154	**,935(**)**	**,914(**)**	**,661(*)**	**,913(**)**
	Cu	-,385	**,782(**)**	,372	,398	**-,763(**)**	**-,814(**)**	-,344	**-,809(**)**
	Cr	,428	**-,797(**)**	**-,709(*)**	,201	**,863(**)**	**,735(**)**	**,789(**)**	**,763(**)**
Reactor 4	Fe	,377	.(a)	-,558	,194	-,016	**,650(*)**	,455	,524
	Mn	,534	.(a)	**-,728(**)**	,088	-,010	**,651(*)**	,494	,430
	Ni	-,423	.(a)	,340	,260	-,401	**-,712(**)**	**-,672(*)**	-,422
	Zn	,069	.(a)	-,329	,142	**-,579(*)**	-,268	-,040	-,571
	Cu	,456	.(a)	-,518	,114	,113	**,609(*)**	,518	,353
	Cr	,382	.(a)	-,518	,023	,184	,310	,444	-,039

** Correlation is significant at the 0.01 level (2-tailed).
* Correlation is significant at the 0.05 level (2-tailed).
a Cannot be computed because at least one of the variables is constant.

Table 5.9. Pearson correlation coefficient

Correlation Coefficient	**Descriptor**
0.0-0.1	trivial, very small, insubstantial, tiny, practically zero
0.1-0.3	small, low, minor
0.3-0.5	moderate, medium
0.5-0.7	large, high, major
0.7-0.9	very large, very high, huge
0.9-1.0	nearly, practically, or almost: perfect, distinct, infinite

According to Table 5.7, significant correlations were found the following parameters:

In terms of Reactors;

1. For Reactor 1 under anaerobic conditions; Fe, Mn, Ni and TOC, SO_4, ORP, pH(reverse), CI, PO_4, CO_3. Zn, Cr and same parameters excluding ORP. Cu and ORP (reverse).

2. For Reactor 2 under anaerobic and aerobic conditions; Fe, Mn, Zn and TOC, SO_4, ORP, pH(reverse), CI, PO_4. Ni and same parameters including CO_3. Cu and TOC, ORP, Cl, CO_3. Cr and ORP, NH_3, CI, PO_4, CO_3.

3. For Reactor 3 under aerobic conditions; Fe, Mn and SO_4 (reverse), NH_3, CI, CO_3. Zn, Cr and SO_4(reverse), ORP (reverse), NH_3, CI, PO_4,CO_3. Cu and SO_4, NH_3 (reverse), CI (reverse),CO_3.

4. For Reactor 4 under aerobic and anaerobic conditions; Fe and CI. Mn and ORP (reverse), Cl. Ni and Cl (reverse), PO_4(reverse). Zn and NH_3 (reverse), Cu and Cl.

As shown organic content, pH, sulfate reduction, ORP, Cl^-, PO_4^{-3}, CO_3^{-2} have significant effects on decrease in metal concentrations of Reactors 1 and 2. On the other hand, organic content and pH of Reactors 3 and 4 do not have influence on metal leaching. Because highly reducing environment confirmed by low ORP values was established in these reactors as soon as waste was loaded to the reactors, it was thought that heavy metals decreased due to precipitation and it could not be observed meaningful correlation between heavy metals and descriptive parameter.

5.4. Gas Analyses

Gas volume and composition were determined as indications of the progression of landfill stabilization processes. While methane and carbon dioxide are the major products of anaerobic conversion of waste, water and carbon dioxide, on the other hand, are the major products of aerobic solid waste decomposition. The results of gas production as daily and cumulative and gas composition are given in Figures 5.59 through 5.67

5.4.1 Gas Production

Daily gas production was measured in the anaerobic reactors by recording the total amount of gas produced in 24 hours. The daily gas production of the anaerobic reactors is given in Figure 5.59. The results can be used for quantitative characterization of reactors performance related to the microbial activity within the reactors. In the start-up period, organics in the reactors are hydrolyzed and the produced organic acids cease gas production. During the intermediate anaerobic degradation stage, methanogenic bacteria slowly start to appear and gas production rate increases (Murphy et al., 1995). After the onset of methane fermentation phase, gas production rates increase initially to their highest values and decrease concomitantly as waste conversion progressed. In this study, all these steps were observed in Reactors 1 and 2. However, since organic matter was completely hydrolyzed and nearly stabilized during aerobic process of Reactor 4, change in gas production was not observed. As can be seen from Figure 5.59, the anaerobic reactor (Reactor 1) exhibited some retardation in terms of gas production, because of the long acidogenesis period as confirmed by high COD concentrations and low pH values. Even though, initial gas production in the anaerobic reactor started on Day 58, steady daily gas production was measured around day 330 and reached to 20 L/day on Day 445 which was the highest value of gas production. Moreover, methane content of biogas was about 48% during these days (Fig. 5.61). In Reactor 2 (anaerobic - aerobic) gas production was observed on Day 92 and reached its peak values between days 148 and 200. The highest volume of gas produced was 17.7 L/day on Day 151. It may be noted from these trends that peak gas production was obtained much earlier in Reactor 2 compared to Reactor 1. Gas production continued in this reactor until the end of operation on Day 295. On the other hand, gas production in aerobic pretreated reactor (Reactor 4) started after the reactor was closed on day 75. Organic matter in this reactor was hydrolyzed aerobically. However, the average gas production did not exceed 2 L/day due to nearly completed stabilization of the readily degradable organic carbon sources.

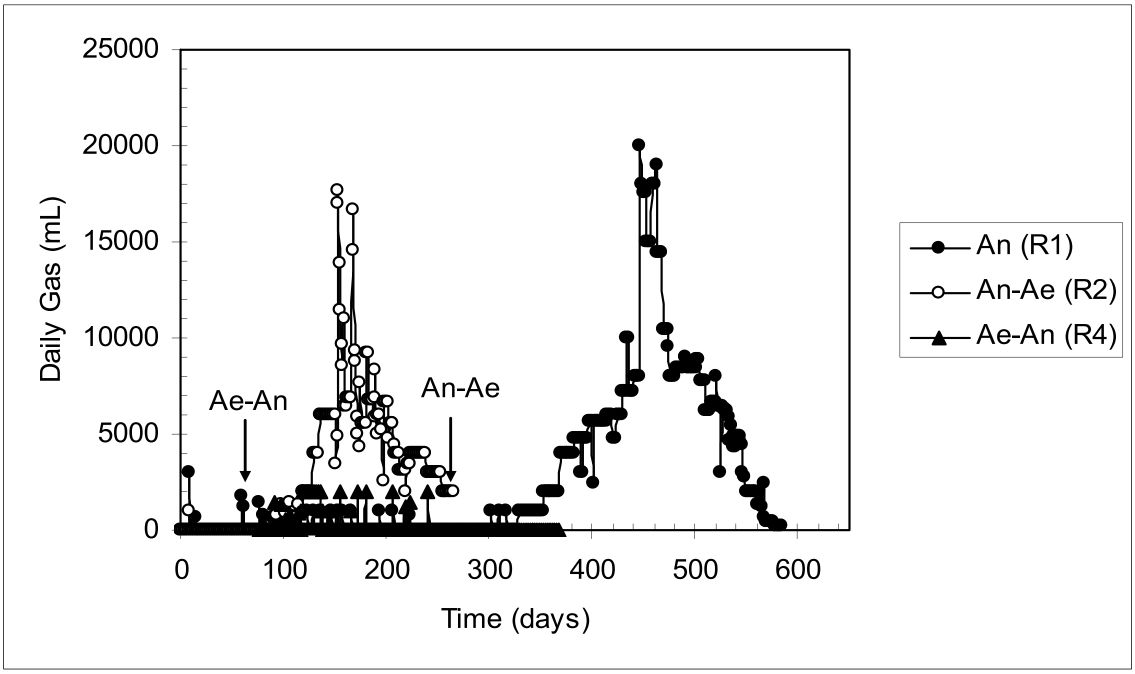

Figure 5.59. Daily Gas Production

Leachate recycle intensified microbial activity by reintroducing volatile organic acids, a principal substrate for methanogens, 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. As expected, this increase got smoother at every reactor after a certain period. The reactors that completed stabilization reached this state earlier due to decreasing amounts of gas production. During the time interval between Days 327 and 583, Reactor 1 displayed gas production, followed by Reactor 2 between Days 116 and 263 and by Reactor 4 between Days 115 and 136.

Cumulative gas production was calculated by summing all of the observed daily gas production within the experimental period. Therefore, the cumulative gas production changed according to daily gas production data. Cumulative gas productions of the reactors are presented in Figure 5.60 and given in Table 5.10. The cumulative gas production in the reactors were recorded as follows; Reactor 1; 1496,9 L, Reactor 2; 752,6 L, Reactor 4; 62,7 L.

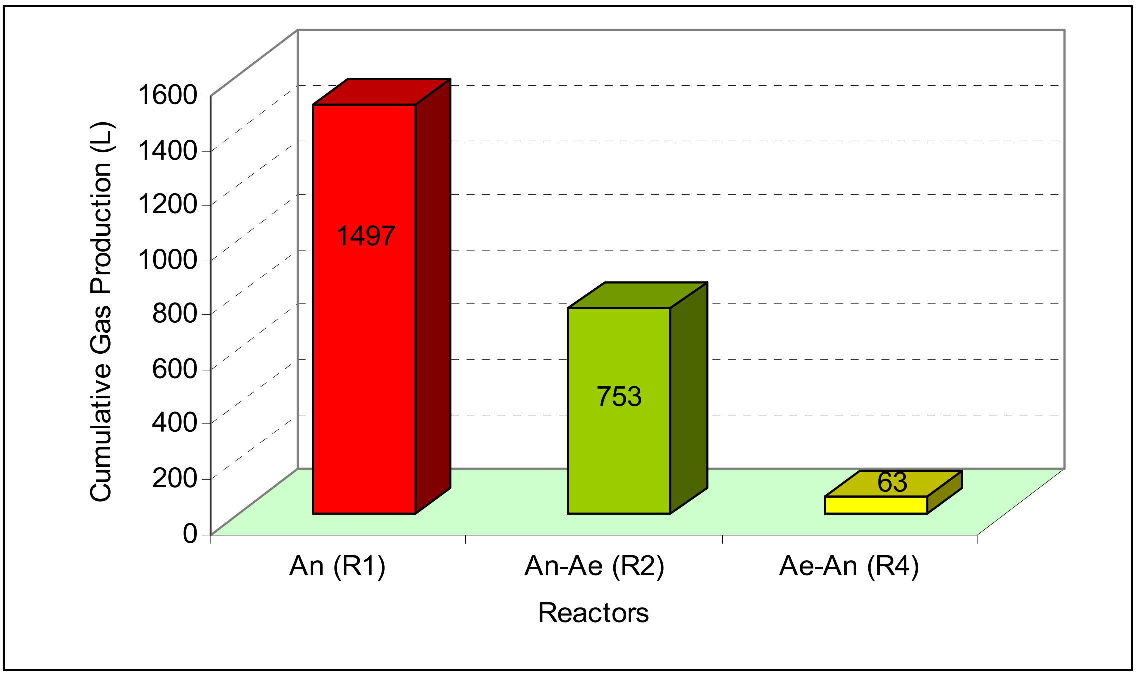

Figure 5.60. Cumulative Gas Production

Table 5.10. Comparison of gas volumes from the reactors

Reactors	Cumulative Gas Production (L)	Maximum Incremental Gas Volume Produced (L)	Time Required to Reach Max. Production (day)
Reactor 1	1496,967	20	445
Reactor 2	752,591	17,7	151
Reactor 4	62,700	2	116

The overall volume of gas produced was much larger in the anaerobic reactor (Reactor 1) than in the other reactors, and the maximum volume of gas produced was also greater for Reactor 1 than for Reactors 2 and 4. Gas generation rates were positively correlated with organic matter and operational conditions. When the influent COD concentration increased from 38,022 mg/L to 70,242 mg/L, anaerobic reactor displayed some retardation of gas production because acidic conditions resulting from the rapid degradation of biodegradable wastes and an accumulation of breakdown products may inhibit or delay methane generation, unless this is buffered by other components of the waste stream. This can ultimately result in the process of “acid souring” where pHs fall below the optimum range in which methanogenesis occurs. After the high COD concentration of Reactor 1 began to use by methanogens, the landfill gas production rate increased to 1 L/ day-kg waste on Day 445. On the other hand, in Reactor 2, COD concentrations were lower than in Reactor 1 and it was not observed any retardation in Reactor 2 due to acid accumulation. In Reactor 2 gas production was also lesser (0.91 L/ day-kg waste on day 151) than in Reactor 1, because the reactor had lower COD concentration and was converted to aerobic conditions while it was operated under anaerobic conditions and produced biogas. In Reactor 4, gas generation rate was the lowest (0.1 L/ day-kg waste on day 116) because organic matter due to the aerobic degradation decreased to 2,580 mg COD/L that is lowest organic content compared to other reactors.

4.1.2 Gas Composition

Methane and carbon dioxide are the principal gases produced during the decomposition of organic fraction of waste under anaerobic conditions and present at approximately 55–65% and 35–45%, respectively, during the stable methanogenic phase (Christensen et al., 1996). In the anaerobic reactor (Reactor 1), methane, at first, was not observed due to the acidogenic conditions (Fig. 5.61). In Reactor 1, the soluble substrates were fermented to carboxylic acids, the pH of the refuse may have decreased rapidly to a point where the methanogens were inhibited. This would lead to the souring of Reactor 1. Nitrogen concentration of 80% was indicative of the reactor in which there was not sufficient production of CO_2 and CH_4 to purge the N_2 from the system. Methane concentration began to appear by day 145 but until day 232 methane concentration was less than 5 %. After this day, it increased rapidly and reached to 50% by composition. Increase in methane production was accompanied by a concomitant decrease in nitrogen and carbon dioxide content. The decrease in nitrogen content was more pronounced because carbon dioxide as well as methane was produced during methanogenesis. Gas composition of the anaerobic reactor during methanogenic phase was 49% CH_4, 43% CO_2, 0.5% O_2 and 7.5% N_2, respectively. Maximum 9 L of methane was generated on day of highest gas production while 80% of COD had been removed. This result is in good agreement with the findings of San and Onay (2001).

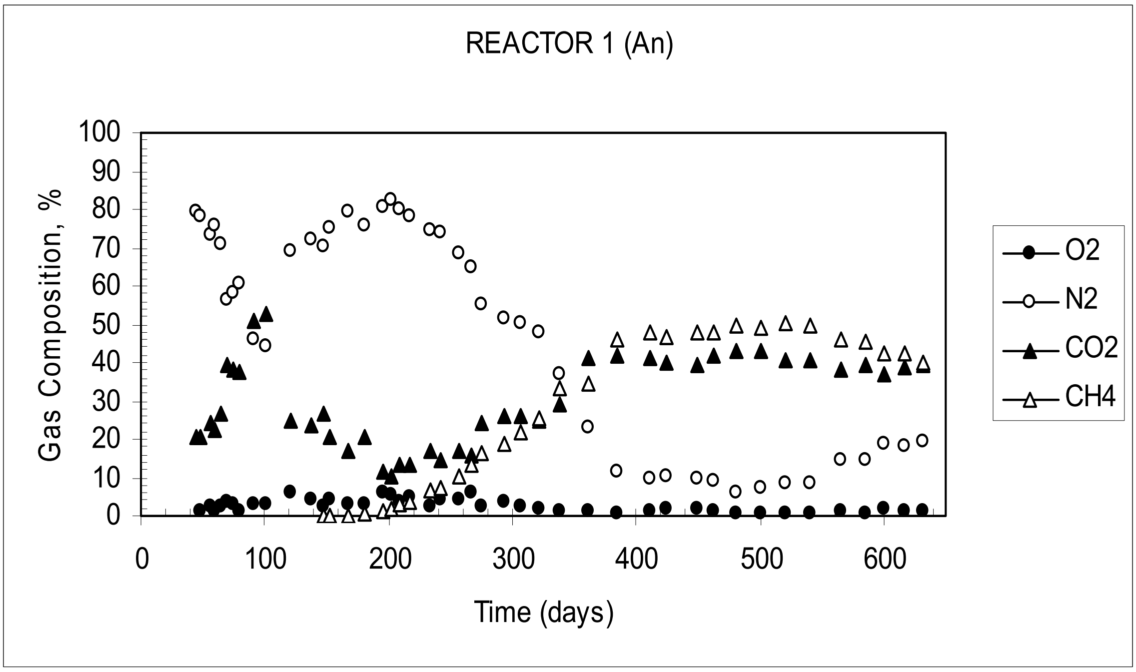

Figure 5.61. Gas composition for Reactor 1

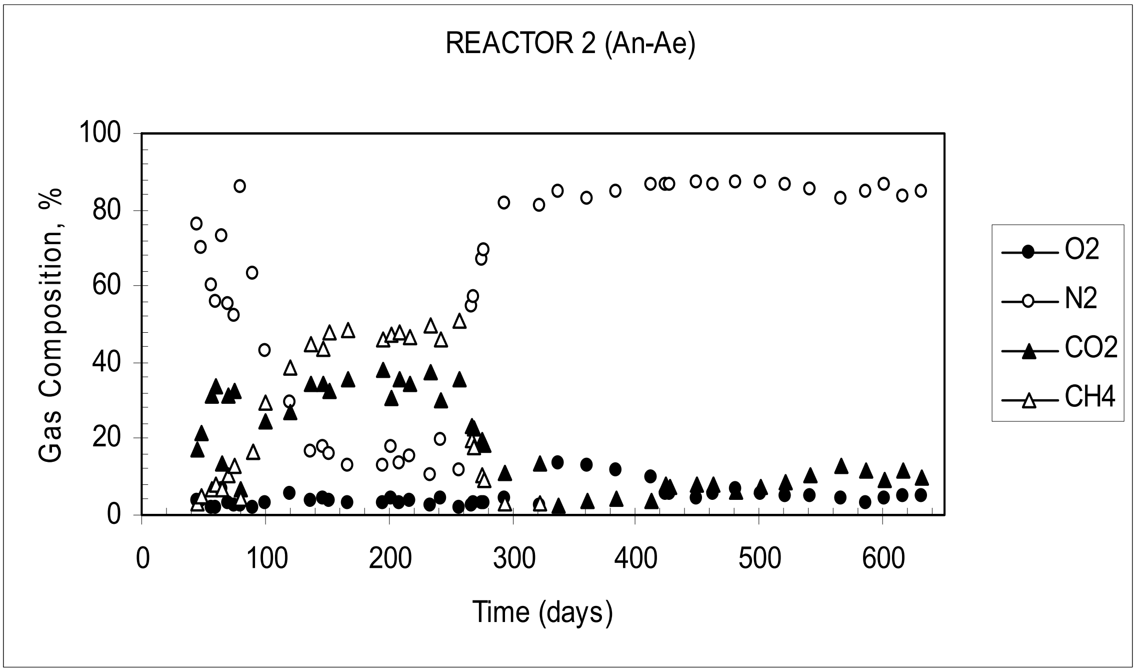

Figure 5.62. Gas composition for Reactor 2

On the other hand, after the onset of methanogenic conditions in Reactor 2, methane percentage reached to about 50% on Day 135 and stayed constant until the aeration period which started on Day 264. The uncontrolled CH_4 emissions from landfills contribute to the greenhouse effect. By shortening the ensuing unprofitable period, aeration of a landfill can save on gas treatment costs. The introduction of aerobic conditions throughout the waste mass reduced methane level rapidly and kept it at a minimum (Read et al., 2001a; Ritzkowski et al., 2006). During the transformation of anaerobic reactor to aerobic, CH_4 and CO_2 percentages were decreased and O_2 and N_2 percentages were increased (Fig. 5.62). In one other related work, Leikam et al., (1997) indicated that methane concentrations in landfill gas could be reduced from 60% to 10–15% in 7–10 days by air injection. In this reactor, methane decreased rapidly from 51% to 19.5% on day 265 after air addition and was observed until day 320. After this day, CO_2, O_2 and N_2 concentrations were only measured. Gas compostion of Reactor 2 on Day 630 was 10.07% CO_2, 5.02% O_2 and 84.91% N_2.

Under aerobic conditions some of the organic carbon in the waste mass is emitted as carbon dioxide and some would be stabilized as carbonates. The intensity of the carbon conversion depends greatly on ambient conditions around the microorganisms (e.g. oxygen concentration, pH, temperature, water content) and the availability of biologically degradable organic substances in the landfilled waste. In this study, gas composition of the aerobic reactor (Reactor 3) was 4.95% CO_2, 14.41% O_2 and 80.64% N_2, at the end of the experiment.

In Reactor 4, there were two degradation processes such as aerobic and anaerobic. Therefore, firstly gas composition was similar to atmospheric air and then, methane generation was observed after the onset of anaerobic conditions. The gas composition on day 78 after the conversion of Reactor 4 from aerobic to anaerobic was 7.4% CH_4, 7.9% CO_2, 4.5% O_2 and 80.26% N_2. High methane percentage was observed during the experiment and reached rapidly to approximately 50% and slowly decreased because organic degradation was terminated in Reactor 4. At the end of study (Day 383), the gas composition was 13.9% CH_4, 14.0% CO_2, 1.5% O_2 and 70.6% N_2.

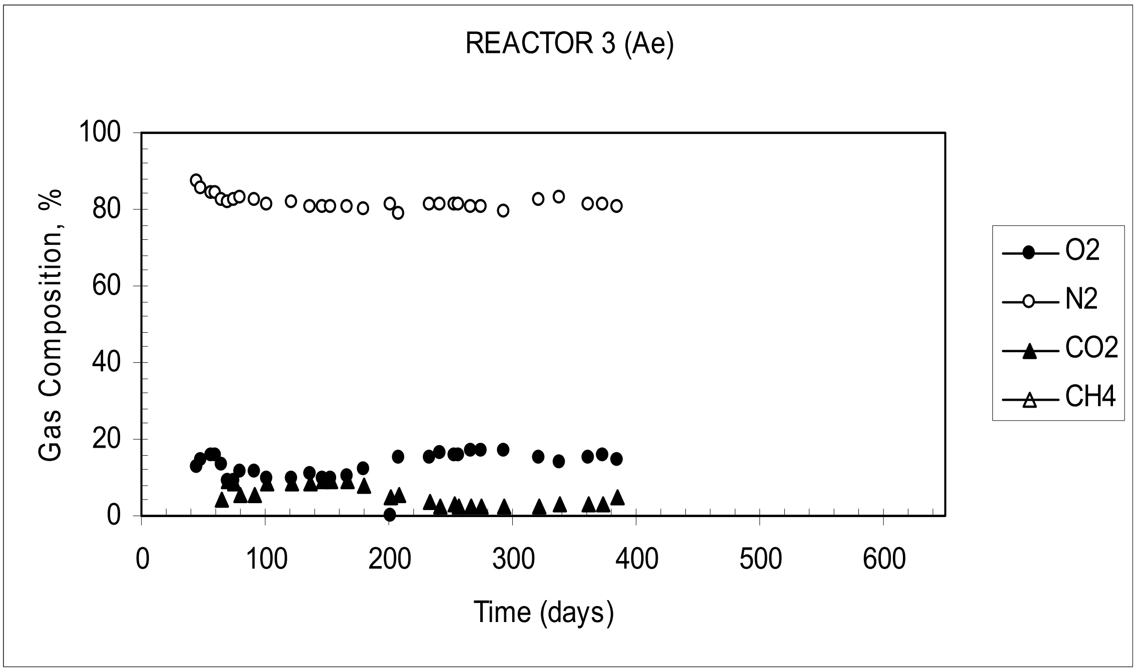

Figure 5.63. Gas composition for Reactor 3

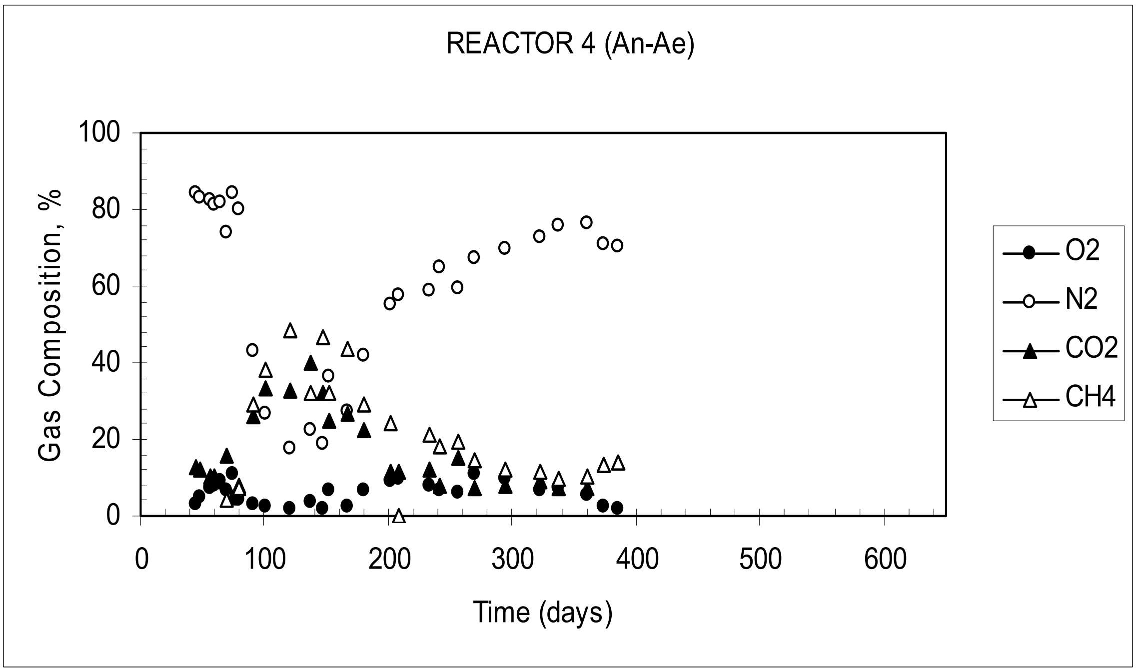

Figure 5.64. Gas composition for Reactor 4

Hydrogen was not measured due to the lack of sensitivity of the gas chromatograph used for this research. The presence of hydrogen was consistent with the depletion of oxygen and production of carboxylic acids which are fermentation intermediates. Its accumulation suggests that there was an imbalance between its generation in fermentative reactions and its utilization by the methanogenic bacteria. The imbalance was manifested by the accumulation of carboxylic acids and the decrease in pH. Disapperance of hydrogen was a result of its utilization by the methanogenic and sulfate reducing bacteria

Figure 5.65 gives the cumulative gas production and composition of Reactor 1 versus time. The cumulative gas production in Reactor 1 was recorded as 1497 L. Cumulative methane and carbon dioxide productions were 690 and 609 L, respectively. Methane yield was determined as 158 L/kg dry solid waste. Other studies have found that the methane yield from landfills is in the range 60–170 L/kg of dry refuse (El-Fadel et al., 1996). Barlaz and Ham (1989) calculated theoretical maximum yield of methane as 373 L CH_4/kg wet solid waste. As can be seen in Fig. 5.65, after conversion of easily degradable organic substances, gas production decreased and gas utilization was no longer possible. In conventional landfills, gas production inevitably slows down until its use as a source of energy is no longer economically viable, but after this point it is still produced in large enough quantities to require treating before it can be emitted to the atmosphere (Rich et al., 2007). On the other hand, the cumulative gas production was 753 L in Reactor 2 (Fig. 5.66). Cumulative methane and carbon dioxide productions were 350 and 252 L, respectively. The enormous differences in cumulative gas productions are a result of conversion of Reactor 2 to aerobic conditions.

In Reactor 4 (Fig. 5.67), the cumulative gas production was recorded as 63 L. Cumulative methane and carbon dioxide productions were 26 and 18 L, respectively. Cumulative gas productions were considerably low when compared to other reactors as a result of excessive aeration and as a direct consequence of almost consumed organic content of Reactor 4.

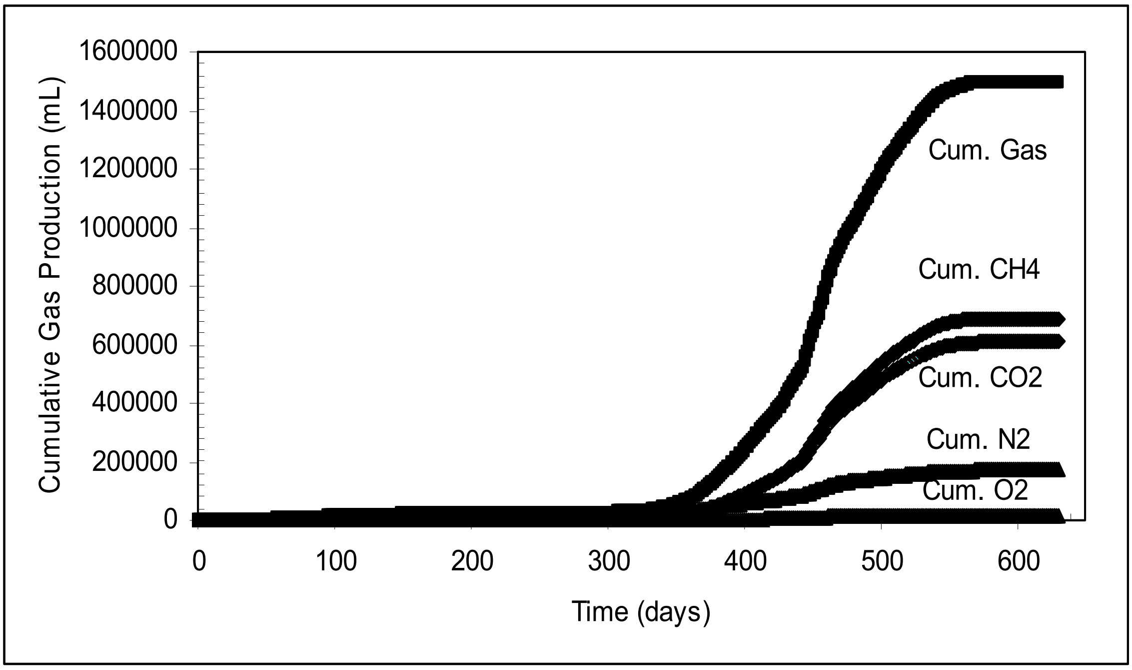

Figure 5.65. Cumulative gas for Reactor 1

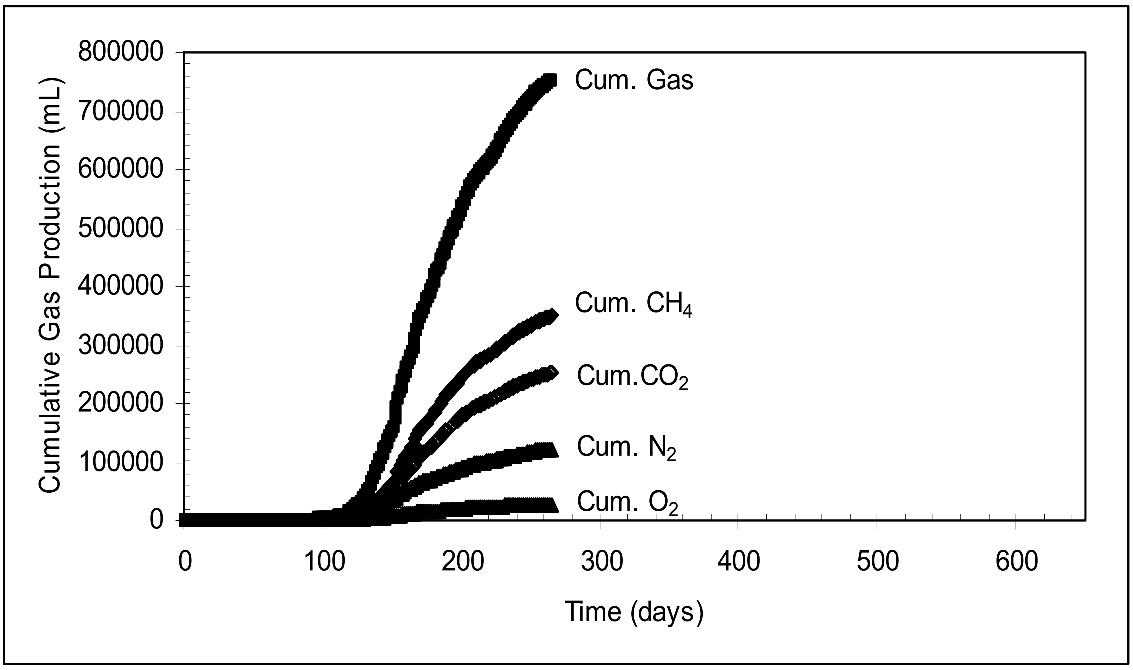

Figure 5.66. Cumulative gas for Reactor 2

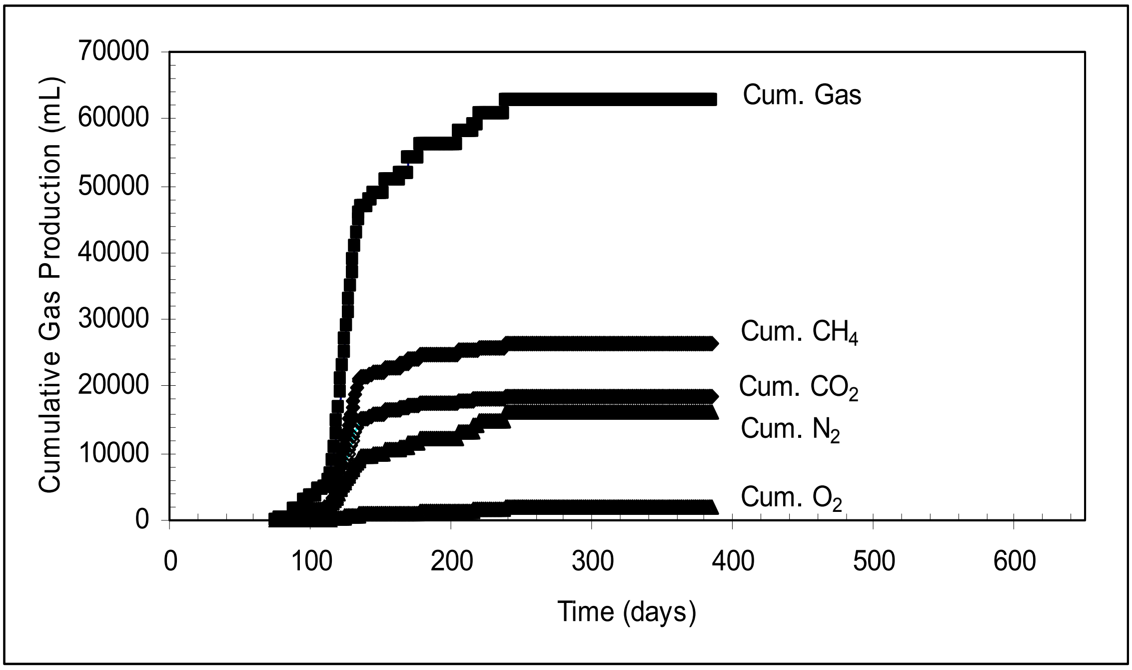

Figure 5.67. Cumulative gas for Reactor 4

5.5. Final Solid Waste Analysis

After the completion of the simulated landfill bioreactor operations, leachate produced by each reactor was allowed to drain prior to the disassembly and waste samples were collected for final analysis. When the stabilized waste was removed from the reactors, visual observations were also made with regard to the physical appearance of the waste (Figure 5.68). Much of the inert materials such as metal, glass and plastic were readily recognizable, as was a considerable amount of cardboard and newsprint, some indicating apparent physical or chemical change. Sections of newspaper were not readable due to the reaction with the leachate over the experimental period. Because the initial waste was shredded by hand, it was difficult to discern other differences in component characteristics, with exception of the greater settlement discussed previously.

After visual inspection, the same analyses that were performed at the start up of the reactors were repeated on the residual waste, including moisture content, ultimate analysis (C,N,H,S,O), density, volatile solids and metals.

Table 5.11 presents the results of the waste analysis for the four reactors. The moisture content of each reactor increased at the end of experiment due to saturation from water additions and leachate recirculation. The moisture content of the bioreactors was suitable to sustain all desirable biological processes. On the other hand, the volatile solids content of the waste samples decreased indicating stabilization throughout the operation of the reactors. The density of waste from the reactors under aerobic conditions (Reactor 3&4) also increased due to the settlement of the waste caused by rapid biological degradation. The other waste constituents decreased throughout the operation of the bioreactors, including carbon, hydrogen, oxygen and nitrogen. The decrease in these compounds indicated waste stabilization during the operation of the reactors. In Table 5.12 the final concentrations of heavy metals are reported. Recalling Table 5.12, it can be observed that the heavy metal concentrations have increased.

Reactor 1 Reactor 2

Reactor 3 Reactor 4

Figure 5.68. Visual observations of discarded solid waste from the reactors

Table 5.11. Characteristics of final waste used as the waste matrix in the landfill bioreactors

Component	**Reactor 1**	**Reactor 2**	**Reactor 3**	**Reactor 4**
Initial Wet Weight (kg)	15.73	15.52	15.31	16.46
Dry Weight (kg)	5.66	5.4	5.19	5.26
Wet Density (kg/m^3)	200	205	295	296
Carbon (%)	37.70	23.77	16.22	16.35
Nitrogen (%)	1.91	1.89	1.11	1.51
Hydrogen (%)	5.42	3.28	1.26	1.45
Oxygen (%)	26.93	31.45	37.15	33.75
Sulfur (%)	-	-	-	-
C/N	19.74	12.58	14.61	10.83
Volatile Solids (%)	47	51	38	61
Moisture Content (%)	64	65	66	68

Table 5.12. Final heavy metal concentrations in solid waste samples

	Reactor 1	**Reactor 2**	**Reactor 3**	**Reactor 4**
Fe (mg/kg)	6576	5283	3728	2874
Mn (mg/kg)	174	142	194	124
Ni (mg/kg)	10	12	11	8
Zn (mg/kg)	143	85	124	79
Cd (mg/kg)	1.1	1.0	0.9	0.8
Cu (mg/kg)	36	35	39	34
Cr (mg/kg)	7	9	7	4
Pb (mg/kg)	27	19	15	18

5.6. Settlement

As MSW biodegrades in landfills, it undergoes settlement due to loading of additional materials on top, loss of strength of individual pieces of refuse due to wetting and biodegradation, and mass loss by biodegradation and leaching. Settlement is of great interest to landfill operators because of its potential to allow disposal of more refuse in a given volume of landfill. However, settlement can also decrease permeability and thus inhibit leachate recirculation and gas flow and production.

In this study, prior to the removal of waste matrix in the reactors, settlement observations concerning the simulated landfill bioreactors were made subsequent to their disassembly after the thermometers and gas meters were disconnected and reactor lids removed. All reactors had settled uniformly across the surface during the experimental period. Settlement or subsidence of MSW is a key parameter that distinguishes between aerobic and anaerobic bioreactor landfills. The depth of the stabilized waste was determined by measuring from the top of waste in the reactor to the surface of the gravel layer. This result was then compared to the measurement initially taken prior to closure as indicated in Table 5.13. Figure 5.69 indicates the depth of waste in the reactor at the end of experiment.

Table 5.13. Net settling or compaction in the reactors

Reactor Identity	Initial Waste Depth, cm	Final Waste Depth, cm	Change in Waste Depth, cm	Settling, %
Reactor 1	86	82	4	5
Reactor 2	88	79	9	10
Reactor 3	86	54	32	37
Reactor 4	89	58	31	35

Reactor 1 Reactor 2

Reactor 3 Reactor 4

Figure 5.69. Visual observations of the settlement in the Reactors 1,2,3 and 4

Based on these measurements, aerobic degradation enhances the rate and extent of subsidence. Higher degree of settlement was achieved in the aerobic bioreactor (Reactor 3) where settlement was about 37% at 374 days. Anaerobic bioreactor (Reactor 1) exhibited settlement about 5% after 630 days. In Reactors 2 and 4, the settlements were measured as 10% and 35%, respectively. Several previous studies have also measured subsidence. The Mountain View Landfill Project in California measured 13–15% settlement with leachate recirculation over a period of 4 years as compared with 8–12% settlement in the control reactor (Buivid et al., 1981). Stessel and Murphy demonstrated 18–30% settling for aerobic bioreactor in laboratory over a 65-day experiment period. Youcai et al. (2002) found the settlement in bioreactors operated under anaerobic conditions was in range of 2.5 to 22.5 % of the initial height of the waste at the end of experiment (300 days). Jin et al. (2006) run experiments in aerobic (18 days) followed by anaerobic conditions for 72 days. They observed that while the settlement of aerobic stage was 20%, the total settlement was 25% at the end of the study. Settlement during actual landfill operations will impact the performance of the final surface grade, surface drainage, roads, gas collection piping system and leachate and air distribution piping system. Settlement impacts can be readily accommodated by the project design. Since settlement in aerobic landfills will be largely complete soon after landfill closure, long-term maintenance costs and the potential for fugitive emissions will be avoided.

5.7. Carbon Balance in the Reactors

Carbon balances were performed on all reactors through elemental analysis. The objective is to determine the total mass of carbon existing in the system after various conversion processes. The equation below outlines the principle of continuity of carbon mass in simple form.

Refused Placed = Mass Leaving in Leachate + Mass Leaving in Gas + Waste Remaining + Mass Transformed to Other Products

This approach can be employed in the studies of input and output fluxes to predict decomposition and to develop limits on the short and long term behaviour of landfills and thus its influence on the environment.

The monitoring of biogas flow rate and composition during the experiment, the measurement of elemental carbon in waste samples at the beginning and the end of experiment as well as in the leachate extracted during the experiment (TOC) enabled the evaluation of carbon mass transfer from the solid to the liquid and gas phase in the different operational conditions. However, it is rather difficult to make a carbon balance in the bioreactors, especially the ones under aerobic conditions due to the immeasurable gas production. Carbon balances of all reactors were calculated to give raw idea about operational conditions and presented at below.

Carbon balances are based on the biodegradable fraction contained in volatile solids.
Biodegradable volatile solids (BVS %) = (VS %) * (Biodegradable faction %) (Speece, 1995).

<u>Reactor 1:</u>

Waste placed =9.56 kg*0.4309*[0.82*0.60]=2.026 kg C
$\sum$ Leachate TOC released= 414 g TOC = 113 g C
$\sum$ Biogas ($CH_4 + CO_2$) measured = 1.299 m^3
CH_4 = 690 liters at STP (0°C and 1 atm) = 0.492 kg CH_4 =0.370 kg C

CO_2 = 609 liters at STP (0°C and 1 atm) =1.196 kg CO_2 =0.326 kg C

Waste remaining = 5.66 kg*0.3770*0.47=1.002 kg C

Reactor 2:

Waste placed =9.95 kg*0.4262*[0.86*0.60]=2.188 kg C

$\sum$ Leachate TOC released= 133 g TOC = 36 g C

$\sum$ Biogas (CH_4 + CO_2) measured = 0.602 m^3

CH_4 = 350 liters at STP (0°C and 1 atm) = 0.25 kg CH_4 =0.188 kg C

CO_2 = 252 liters at STP (0°C and 1 atm) =0.50 kg CO_2 =0.135 kg C

Waste remaining = 5.4 kg*0.2377*0.51=0.655 kg C

Reactor 3:

Waste placed =7.22 kg*0.4541*[0.84*0.60]=1.652 kg C

$\sum$ Leachate TOC released= 7 g TOC = 1.9 g C

Waste remaining = 5.19 kg*0.1622*0.38=0.320 kg C

Reactor 4:

Waste placed =7.22 kg*0.4846*[0.84*0.60]=1.763 kg C

$\sum$ Leachate TOC released= 10 g TOC = 2.7 g C

$\sum$ Biogas (CH_4 + CO_2) measured = 0.044 m^3

CH_4 = 26 liters at STP (0°C and 1 atm) = 0.0186 kg CH_4 =0.014 kg C

CO_2 = 18 liters at STP (0°C and 1 atm) =0.036 kg CO_2 =0.0098 kg C

Waste remaining = 5.26 kg*0.1635*0.61=0.525 kg C

The calculations are also presented in Figures 5.70, 5,71, 5,72 and 5,73. As shown in figures, the highest transfer of carbon into the leachate phase occurred for Reactor 1, where a cumulative value of 0.113 kg C was calculated after 630 days. Around 11% of carbon in the waste sample was transferred into leachate. Reactor 2 follows Reactor 1 in terms of high carbon transfer into leachate. In Reactors 3 and 4 under aerobic conditions, carbon in leachate is low due to rapid degradation and conversion of carbon to carbon dioxide.

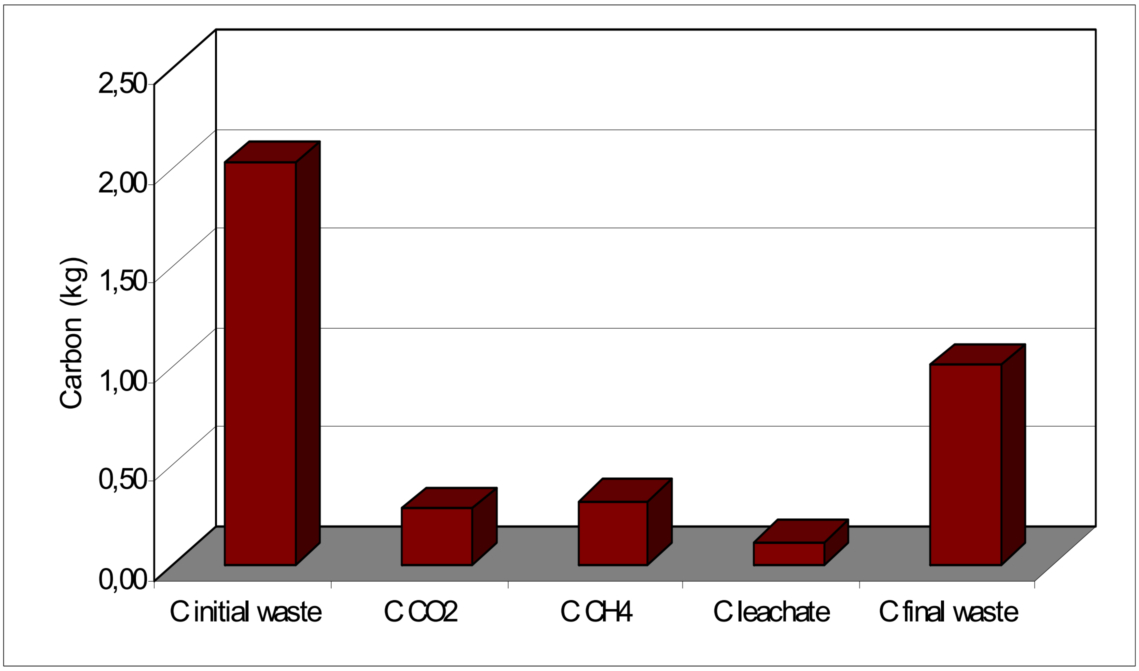

Figure 5.70 Carbon compounds in Reactor 1

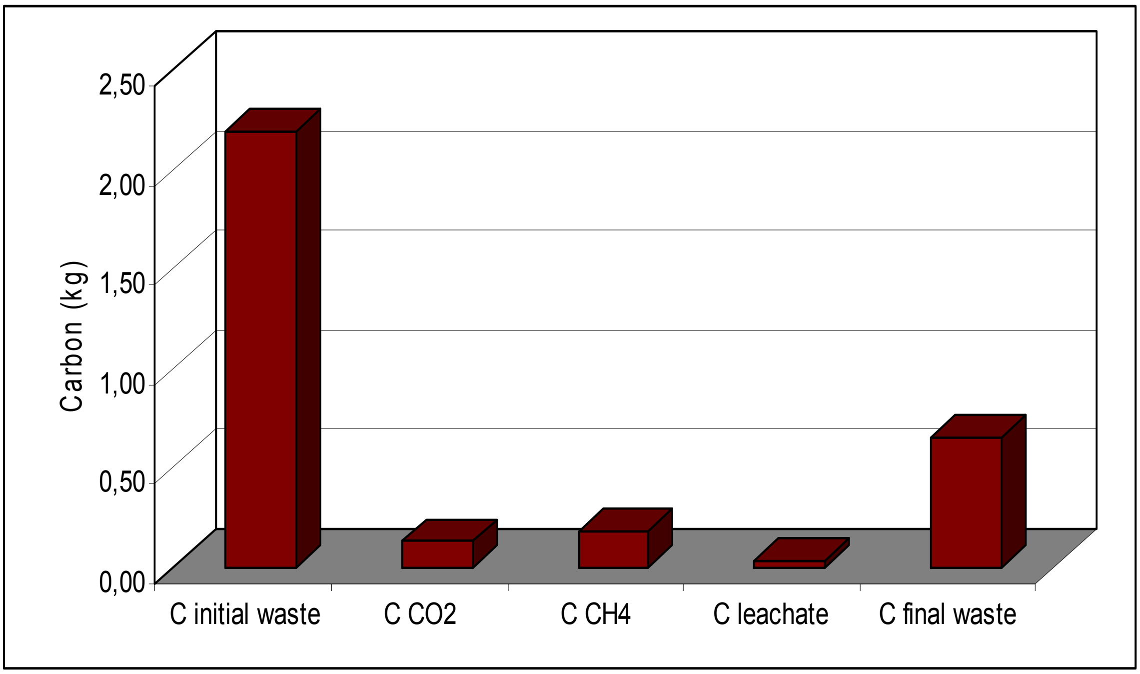

Figure 5.71 Carbon compounds in Reactor 2

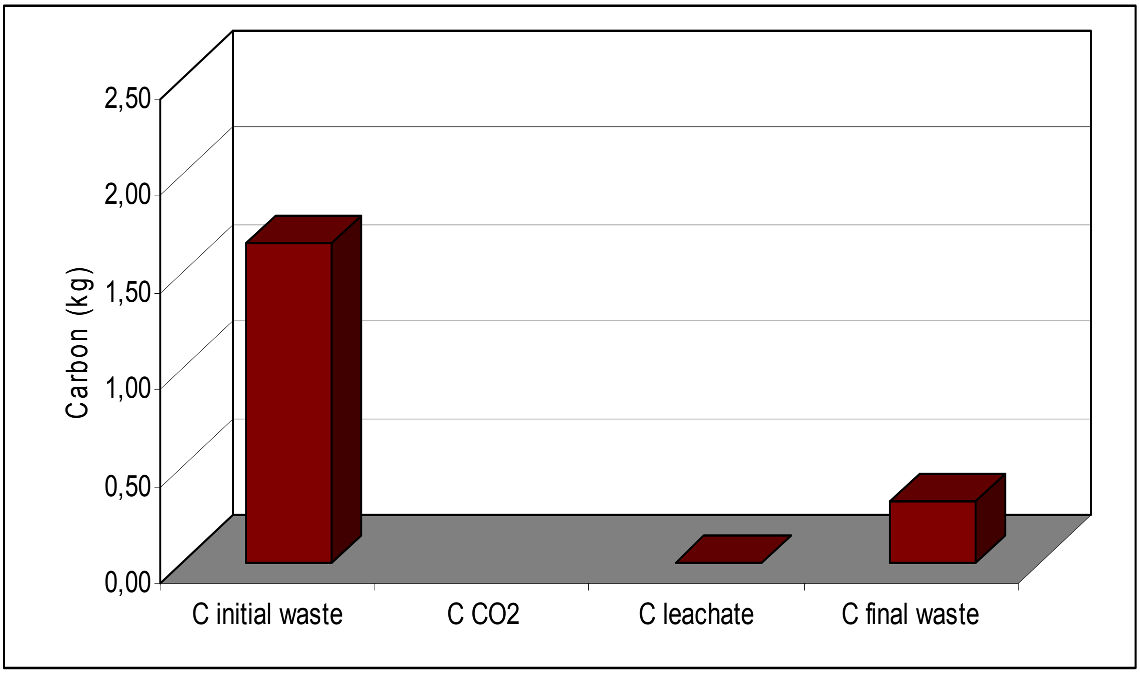

Figure 5.72 Carbon compounds in Reactor 3

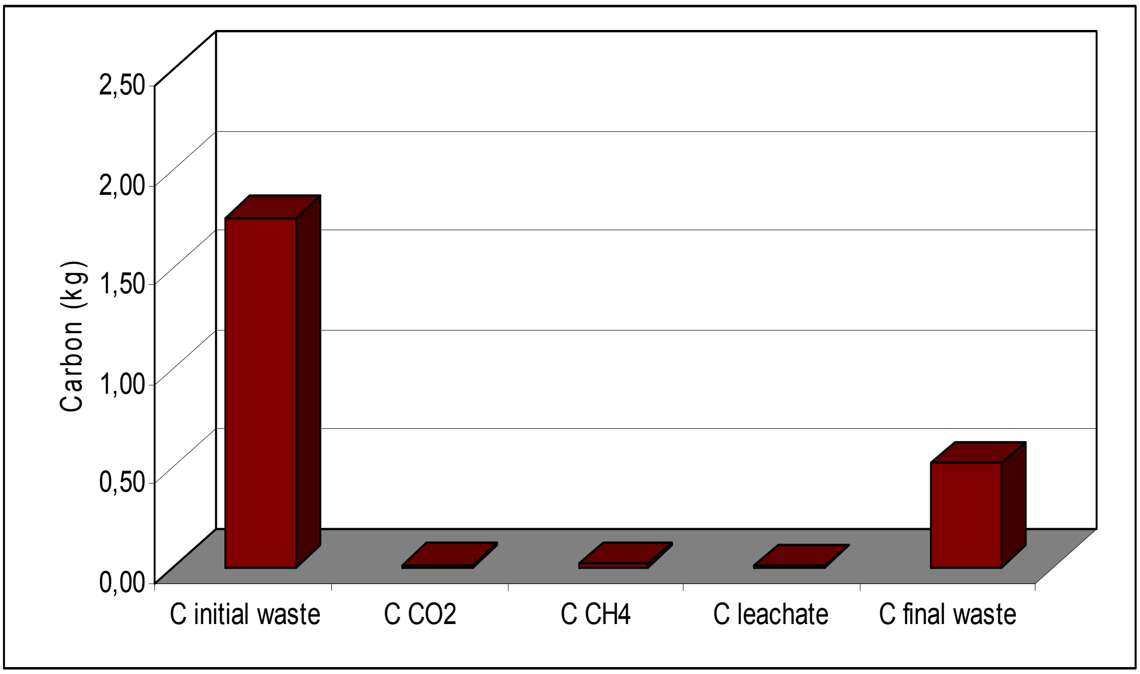

Figure 5.73 Carbon compounds in Reactor 4

Carbon release in the gas phase is considered for only anaerobic reactors because gas generation in the reactors under aerobic degradation could not measured due to air flow addition. From figures, the lowest gasification occurred in the Reactor 4, where total amount of carbon measured in gas phase was about 0.024 kg C due to rapid degradation of organic carbon in aerobic phase. Higher values, around 0.69 and 0.32 kg C respectively, were measured for the other reactors 1 and 2 under anaerobic conditions.

5.8. Carbon, Nitrogen and Heavy Metal Recovery

Recovery analysis of main elements in the reactor was made by using initial and remaining elements of waste to understand removal. Recovery of carbon, nitrogen and heavy metals are given in Figure 5.75 through 5.79.

Figure 5.74 and 5.75 indicates change in carbon and nitrogen of the reactor. From the figures, carbon masses existing the reactor were 4.20 kg for Reactor 1, 4.24 kg for Reactor 2, 3.27 kg for Reactor 3 and 3.50 kg for Reactor 4 which resulted in carbon recoveries of 50%, 70%, 74% and 75%. On the other hand, initial nitrogen masses were 0.14 kg for Reactor 1, 0.16 kg for Reactor 2, 0.11 kg for Reactor 3 and 0.11 kg for Reactor 4 which resulted in nitrogen recoveries of 24%, 37%, 46% and 28%.

Heavy metal masses of solid waste samples taken from aerobic and anaerobic landfill reactors are shown in Figs. 5.76, 5.77, 5.78 and 5.79, respectively. All heavy metal masses are increased at the end of study. The increase may be attributed to the weight loss of solid waste during the digestion process through mineralization of organic fractions (Ciavatta et al., 1993). Fang and Wong (1999) and Arıkan (2003), determined similar results in their studies and suggested that the increase in metal concentrations generates as a result of the mass loss in landfills.

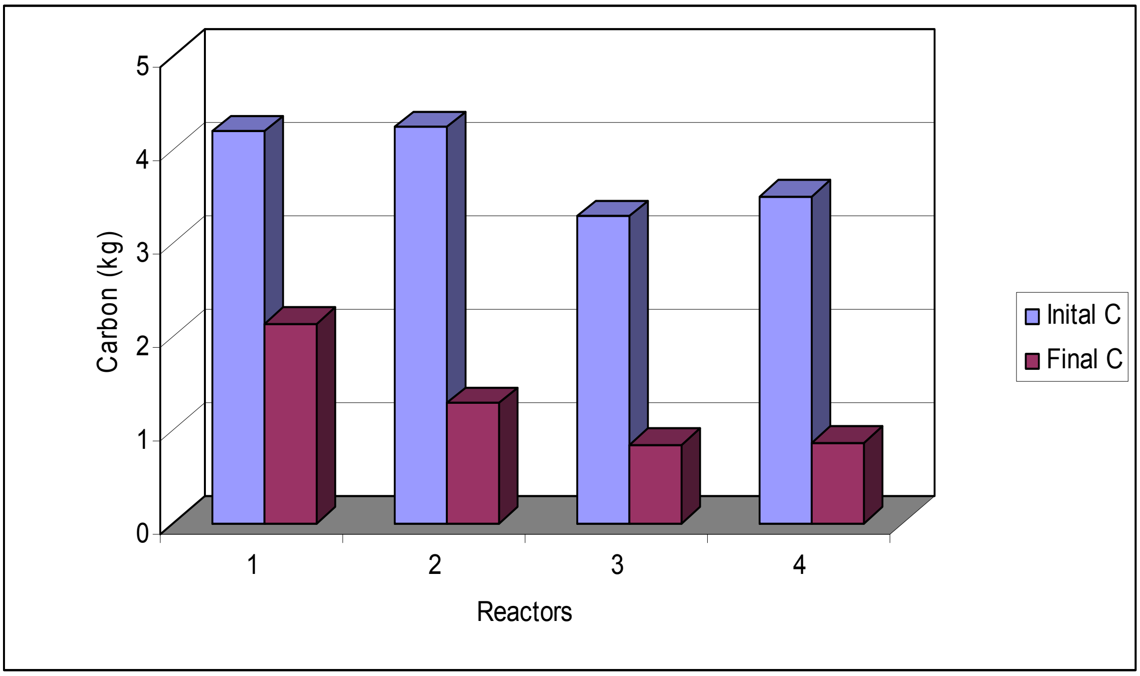

Figure 5.74 Change in carbon

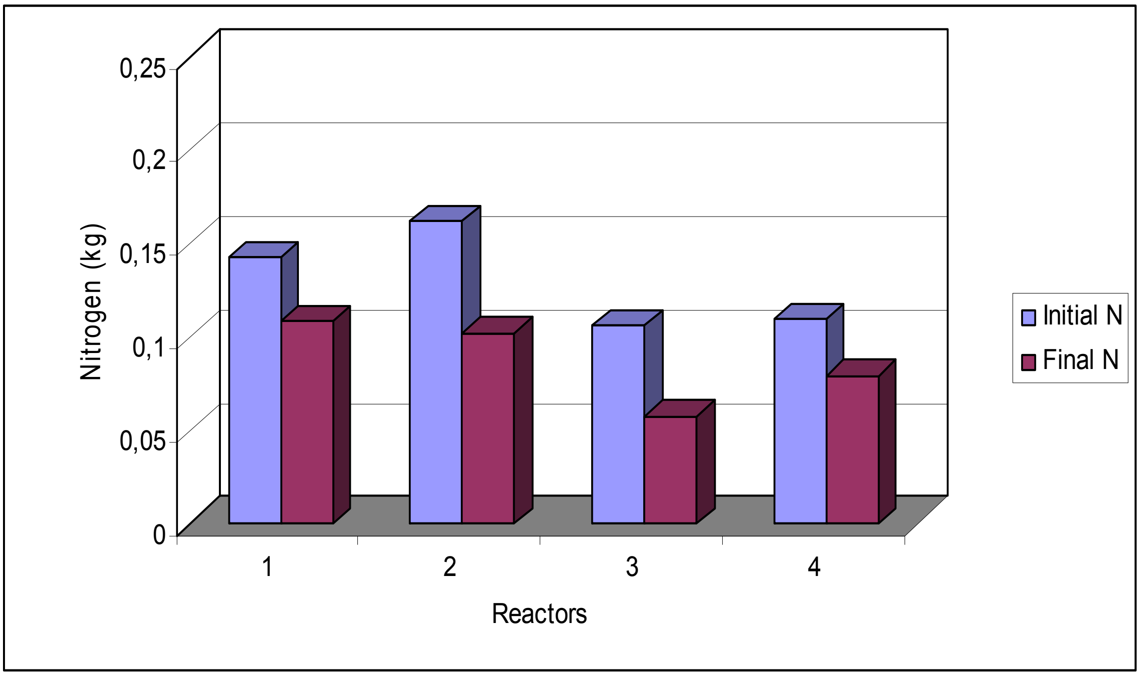

Figure 5.75 Change in nitrogen

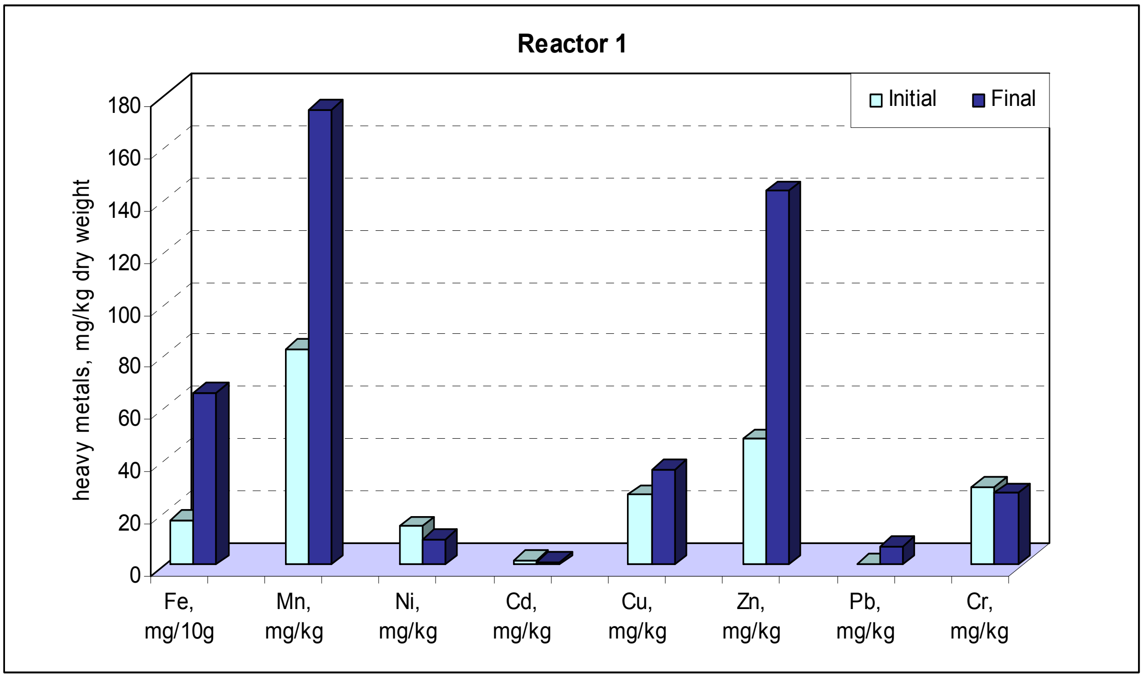

Figure 5.76 Change in heavy metals for Reactor 1

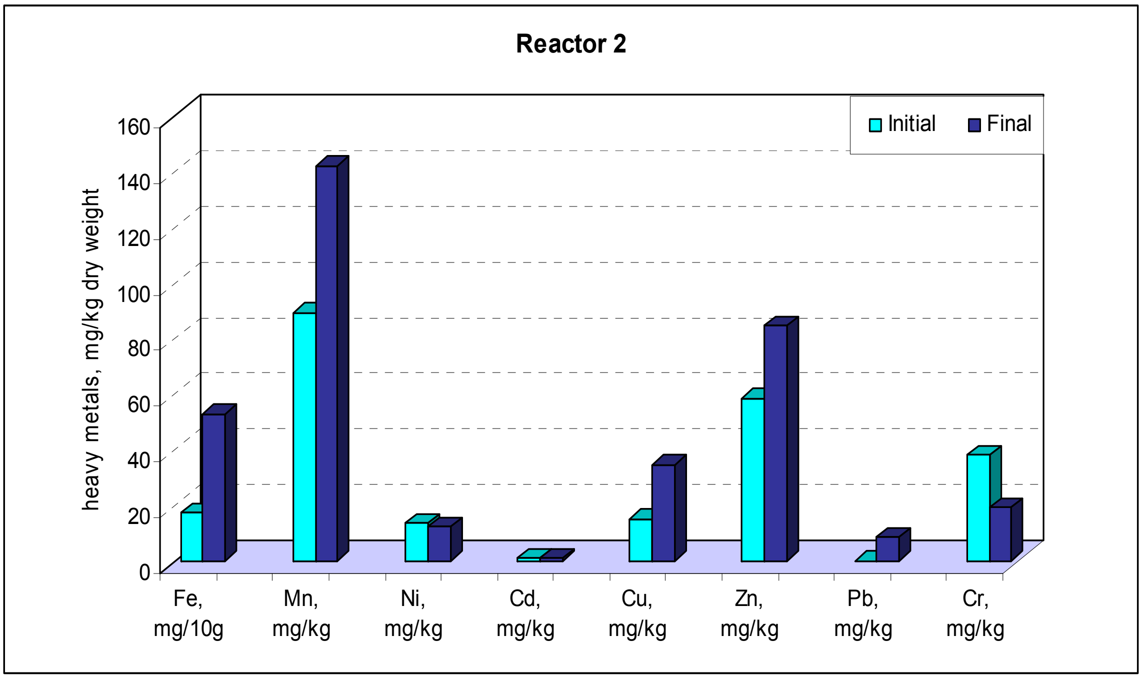

Figure 5.77 Change in heavy metals for Reactor 2

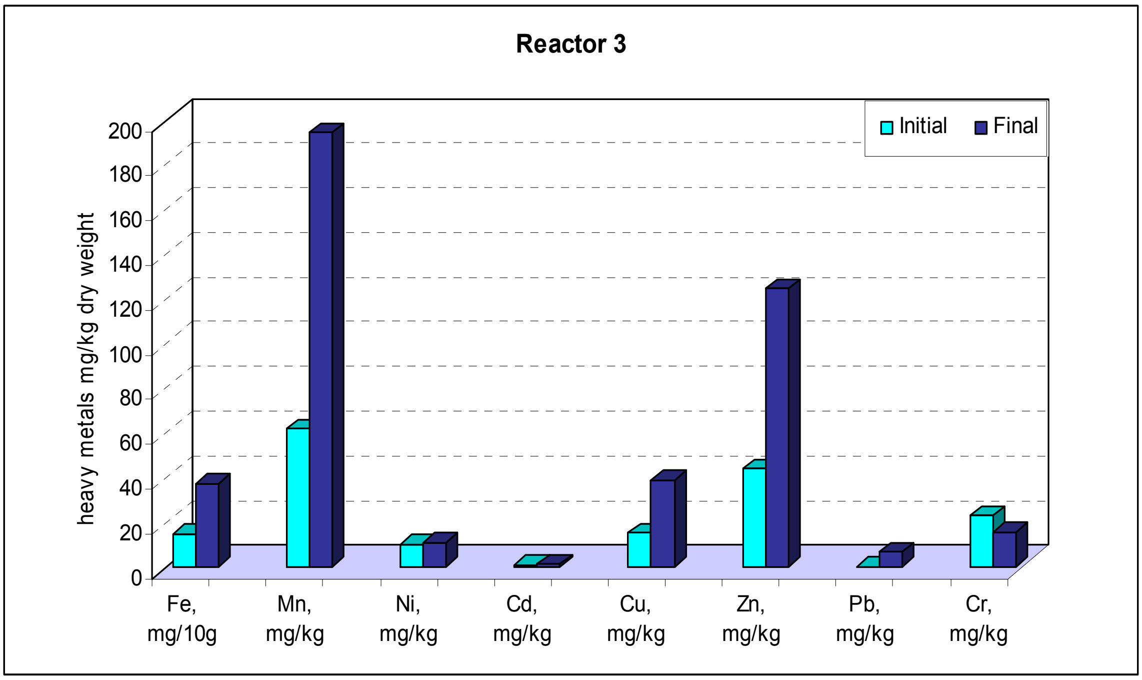

Figure 5.78 Change in heavy metals for Reactor 3

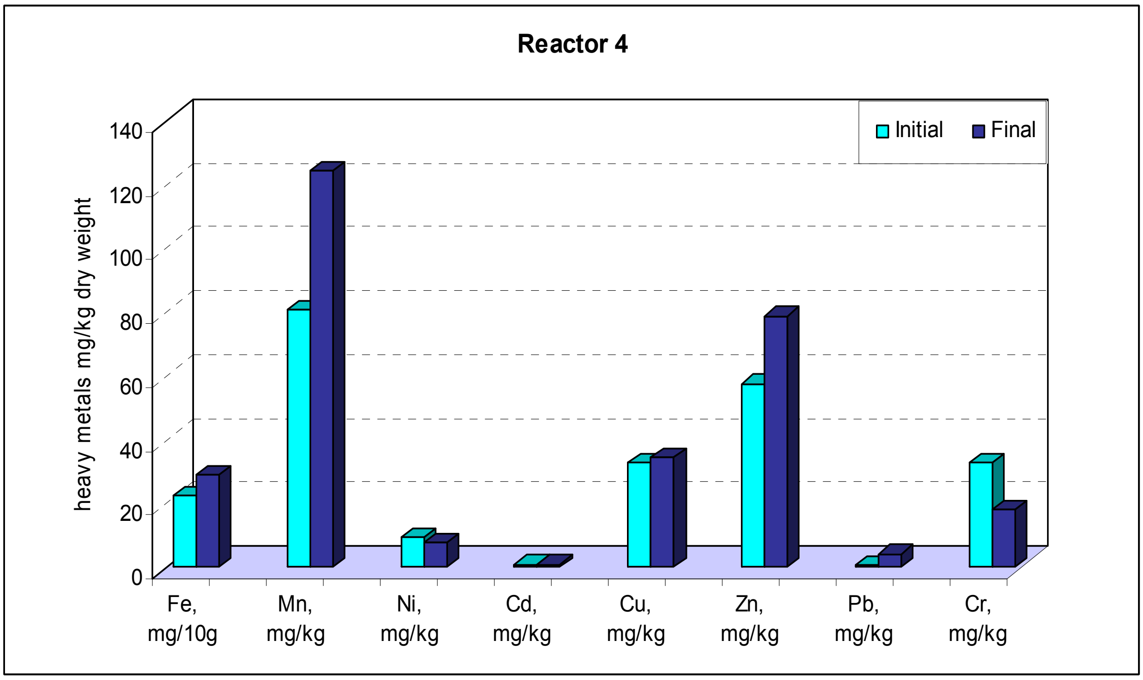

Figure 5.79 Change in heavy metals for Reactor

5.9. Economic Evaluation of Bioreactor Landfill Systems under Aerobic and Anaerobic Conditions

This chapter addresses the economic aspects of employing aerobic and anaerobic degradation processes as an alternative landfill management strategy. Since this thesis investigated the advantages of aeration at landfill sites, and developed new design and operational plans for sustainable solid waste management, it was decided to complete the effort with an examination of the economic feasibility of applying these technologies.

The economical anaysis was mainly conducted through three different stages, namely construction stage, operational stage and closure stage. The costs for each stage were estimated separately in order to have a clear impression of the development, operational and closure costs of the simulated reactor landfills.

The capital costs include

- land acquisition,
- site development,
- liner construction,
- leachate management system,
- gas management system,
- air injection management system,
- surface water management system,
- monitoring well,
- access roads,
- office and weight bridge,
- car wash & garage

Components of operating costs;

- personel
- daily soil

- leachate analysis
- machinery
- utilities
- maintenance
- others

Components of closure and post-closure costs;

- final top cover
- vegetations
- maintenance
- monitoring (10 years for aerobic, 25 years for anaerobic bioreactors)

In all analyses, however, no consideration was given to costs that are the same under all scenarios such as liner construction, land acquisition, site development.

The Case Study;

Istanbul Metropolitan Municipality operates two modern municipal solid waste landfills in the city; Odayeri/Göktürk on the European side and Kömürcüoda/Karakiraz Village on the Anatolian side. The site selected herein is analogous to that located in Odayeri (Göktürk), which comprises 75 heactares and serves 8 thousand tones of garbage that is being collected daily (http://www.istac.com.tr/faaliyetler-eng.asp?faal=duzenlidepolama).

In this study, disposal areas simulating the reactors are designed and constructed of approximately 10 heactares and each is operated for a five-year period. Accordingly, a 10 heactare cell was selected and assessed for the purpose of providing an economic comparison of aerobic and anaerobic degradation processess. Assuming 10 m average depth, the space capacity of this cell is:

$V = 100\ 000\ m^2 \times 10\ m = 1\ 000\ 000\ m^3$

Therefore, the weight carrying of the cells can be obtained by using average 233 kg/m^3 solid waste “in-place” density which is obtained during reactor loading as:

1 000 000 m^3 x 233 kg/m^3 = 233 000 ton

Knowing that the operational phase of the cell is about five years, the filling capacity at the cell is determined as;

233 000 tons x (1/5) (1/year) x (1/52)(year/week) x (1/7)(week/day)= 128 ton/day

Leachate Generation

The production of leachate from municipal sanitary landfills is an important environmental concern. Many factors such as annual precipitation, runoff, infiltration, evaporation, transpiration, freezing, waste composition, waste density, initial moisture content and depth of the landfill affect the amount of leachate generated. Water Balance Model was selected to evaluate the potential generation of leachate from the simulated landfill area. The analysis of the water balance is also carried out further to predict leachate production in completed landfill areas.

The water balance method involves summing the amount of water entering the landfill and subtracting the amounts of water lost from landfill to predict leachate

$$\text{Leachate}=P-SR-SMS-AET \tag{5.17}$$

Where,

P=precipitation; SR=surface runoff; SMS= change in soil moisture storage; AET= actual evapotranspiration

Daily cover to be used for simulated landfill in İstanbul was assumed as sandy loam without grass having a slope of 2%. The runoff coefficient range for the daily cover having these characteristics is in the range of 0.06-0.14 with a typical value of 0.1 (Tchobanoglous,1993).

Table 5.14. Water percolated through daily cover

Month	Jan	Feb	Mar	Apr	May	Jun	Jul	Au	Sep	Oct	Nov	Dec	Annual mm/year
P	106	82.4	66.6	48.4	38	33.9	32.9	34.8	72.2	85.5	103.5	125.6	829.8
PET	28.8	29.2	37.6	51.1	65.8	92.7	125.4	125.8	96.2	56.3	40	35.2	784.1
C	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	
R/O	10.6	8.24	6.66	4.84	3.8	3.39	3.29	3.48	7.22	8.55	10.35	12.56	82.98
I	95.4	74.16	59.94	43.56	34.2	30.51	29.61	31.32	64.98	76.95	93.15	113.04	746.82
I-PET	66.6	44.96	22.34	-7.54	-31.6	-62.19	-95.79	-94.48	-31.22	20.65	53.15	77.84	
APWL	0	0	0	-7.64	-39.24	-101.4	-197.2	-291.7	-322.9	0	0	0	
ST	100	100	100	92.39	66.72	35.16	13.11	4.95	3.59	100	100	100	
Dif ST	0	0	0	-7.61	-25.67	-31.56	-22.05	-8.16	-1.36	96.408	0	0	
AET	28.8	29.2	37.6	51.17	59.87	62.07	51.66	39.48	66.34	56.3	40	35.2	
PERC	66.6	44.96	22.34	0	0	0	0	0	0	0	53.15	77.84	264.89

Table 5.15. Water percolated through final cover

Month	Jan	Feb	Mar	Apr	May	Jun	Jul	Au	Sep	Oct	Nov	Dec	Annual mm/year
P	106	82.4	66.6	48.4	38	33.9	32.9	34.8	72.2	85.5	103.5	125.6	829.8
PET	28.8	29.2	37.6	51.1	65.8	92.7	125.4	125.8	96.2	56.3	40	35.2	784.1
C	0.22	0.22	0.22	0.22	0.22	0.22	0.22	0.22	0.22	0.22	0.22	0.22	
R/O	23.32	18.128	14.652	10.648	8.36	7.458	7.238	7.656	15.884	18.81	22.77	27.632	182.556
I	82.68	64.272	51.948	37.752	29.64	26.442	25.662	27.144	56.316	66.69	80.73	97.968	647244
I-PET	53.88	35.072	14.348	-13.35	-36.16	-66.26	-99.74	-98.66	-39.88	10.39	40.73	62.768	
APWL	0	0	0	-13.35	-49.51	-115.8	-215.5	-314.2	-354	0	0	0	
ST	100	100	100	87.1	60.1	30.3	10.8	3.93	2.61	100	100	100	
Dif ST	0	0	0	-12.9	-27	-29.8	-19.5	-6.87	-1.32	97.39	0	0	
AET	28.8	29.2	37.6	50.652	56.64	56.242	45.162	34.014	57.636	56.3	40	35.2	
PERC	53.88	35.072	14.348	0	0	0	0	0	0	0	40.73	62.768	206.798

In the design, run off coefficient of daily cover was selected as 0.1 Final cover to be used for simulated landfill was assumed as silty loam with grass having a slope of 2%. The runoff coefficient range for the final cover having these characteristics is in the range of 0.17-0.25 with a typical value of 0.22. Runoff coefficient of final cover was selected as 0.22.

The leachate generation projected by water balance model is 265 mm/year. For the simulated landfill area, the annual leachate generation is calculated as below:

Area=10 ha =100 000 m^2

Annual Leachate Generation= 265 mm/year *(1m/1000 mm)*100 000 m^2=26,500 m^3/year

And the total volume of water infiltrated in a five-year period (filling operation) is:

26,500 m^3/year* 5 year=132 500 m^3

After closure, the rate of water infiltration reduces. The annual leachate generation rate from the landfill after closure can be estimated as:

207 mm/y *(1m/1000 mm)*100 000 m^2=20,700 m^3/year

For 30 years leachate production= 5 year *26,500 m^3/year + 25 year *20,700 m^3/year= 650,000 m^3

For 15 years leachate production= 5 year *26,500 m^3/year + 10 year*20,700 m^3/year=339,500 m^3

Leachate Management ;

The leachate generated at the site is collected through a drainage network at the bottom of landfill, contained in storage tanks and then pumped into the landfill. The recirculation operation is performed via a surfacial cascade-type perforated network, and a system of vertical injection wells.

Based on the estimated leachate quantity, external leachate storage may be needed during early phases of a bioreactor landfill operation (years 1 and 2) when the leachate collection system is not covered by the waste, in situ storage does not provide complete moisture absorption by the waste and a dedicated treatment zone is not fully developed to utilize its entire volume to treat leachate. Generally, a storage capacity for about 1 month period is required at the site. Two storage tanks of a total holding capacity equal to 2,000 m^3 is needed for this project.

The economic analysis of leachate recirculation system, as recommended at this site, includes construction, operation and leachate disposal cost, respectively.

Leachate recirculation promotes reuse of nutrients and bacteria in the waste mass and rapidly renders the leachate less harmful. This leads to greatly reduced leachate treatment costs. More specifically, leachate recirculation typically costs less than $ 0.01 per galon ($ 2.65/m^3) while on-site leachate treatment and transportation to an off-site disposal facility range from $ 0.03 to $ 0.15 per galon ($7.94/$m^3$-$39.7/m^3) (http://www-esd.lbl.gov/ECO/smart_store/benefits.html). Therefore, the treatment cost associated with the in-situ method is small and at the lower end of range of reported leachate treatment costs. Based on the cost information in Table 5.16, on-site leachate treatment ranges from $0.004 – 0.18/gal ($1.06-47.55/m^3), while off-site leachate treatment ranges from $0.06 – 0.40/gal ($15.85- 106/ m^3) (Berge, 2006).

Table 5.16.Leachate treatment costs (Berge, 2006)

Source	Description of Leachate Treatment Method	Leachate Treatment Cost ($/m^3)
General Paper Bioreactor	Costs to haul and treat leachate based on information provided by Florida Solid Waste Manager	16-38
Polk County	Cost to haul and treat leachate	29
Yolo County CA	Cites a general disposal cost	5
Countryside Landfill Illinois	Cost includes hauling and treating of waste	19
Darebin Parklands	Cost to pump to sewer and treat leachate	110
Fauquier County Landfill	Cost to transport and treat leachate	48
Essex-Windsor Regional Landfill	Cost to transport and treat leachate (POTW is 15 miles away)	17
Case Study in Georgia	Cost of off-site treatment	32
Buncombe County Landfill, NC	Cost to transport and treat leachate	110
Waste Management Site	Costs are based on several ex-situ, on-site treatment methods, including ex-situ nitrification tank, SBR and wetland units	1.1-5
Conestoga Landfill	Costs based on on-site treatment using different biological and chemical methods	8-13
Orchard Hill Landfill, Michigan	Cost of on-site treatment cost, no transportation added	13

Gas Generation

Gas generation capacity of simulated landfill was estimated by using EPA's LandGEM program (US EPA, 1998). The model assumes that gas production will be highest upon initial placement of waste in the landfill (after a certain negligible lag period during which anaerobic conditions are formed). The rate then decreases exponentially (i.e., undergoes first order decay) as the availability of degradable organic carbon decreases. The model equation is described briefly below (Benson et al, 2007) :

$$Q_{CH4} = W\ L_0 k e^{-kt} \qquad (5.18)$$

Where;

Q_{CH4}=annual methane generation in the year of the calculation, m^3/year

W= annual waste mass acceptance rate, ton/year

L_0=ultimate CH_4 yield per wet mass of waste, m^3/ton

k= methane generation rate constant, $year^{-1}$

The five k values used by LandGEM are shown in Table 5.17. Arid area landfills are located in areas that receive less than 635 mm of rainfall per year. The default k value is the CAA k value for conventional landfills.

Table 5.17. Values for the methane generation rate (k)

Default type	**Landfill type**	**k value ($year^{-1}$)**
CAA	Conventional	0.05 (default)
CAA	Arid Area	0.02
Inventory	Conventional	0.04
Inventory	Arid Area	0.02
Inventory	Wet (Bioreactor)	0.7

Input

LANDFILL CHARACTERISTICS

Landfill Open Year	2005
Landfill Closure Year (with 80-year limit)	2009
Landfill Capacity	233 000 ton

MODEL PARAMETERS

Methane Generation Rate, k	0,7 year^{-1}
Potential Methane Generation Capacity, Lo	170 m^3/ton
NMOC Concentration	2.400 ppm$_v$ as hexane
Methane Content	50 % by volume

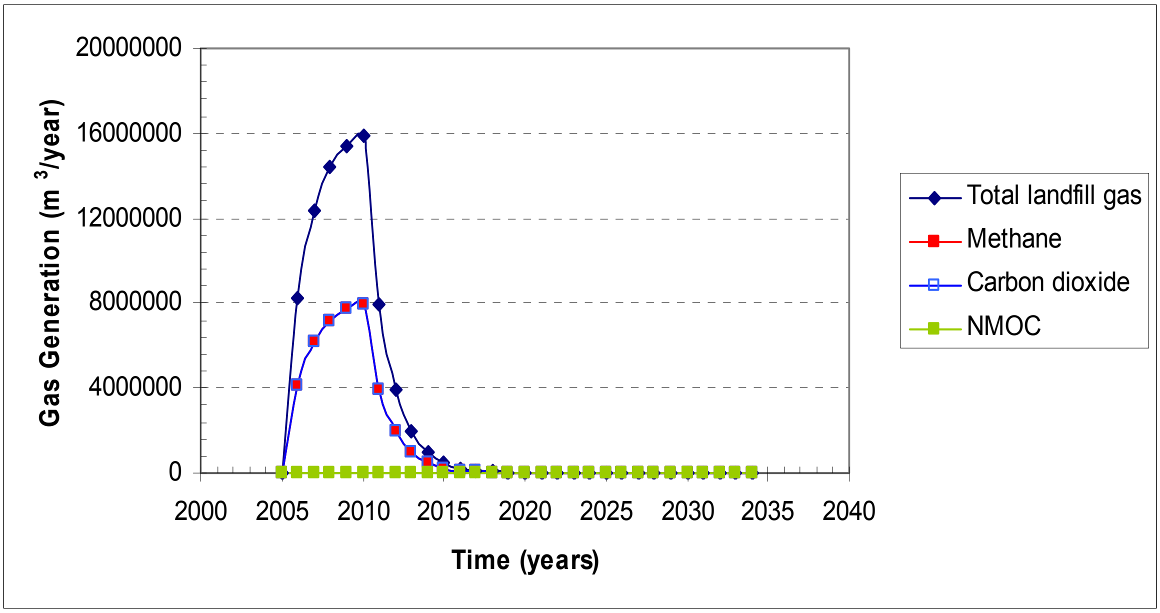

Figure 5.80. Gas generation capacity of simulated landfill

Statistics

82,025,044.73 m^3 LFG in 30 years.

Total landfill gas
Avg: 2,734,168.16 m^3/y Max: 15,909,620.76 m^3/y (Year:2010)

Methane - CH_4
Sum:41,012,522.37 m3 Avg: 1,367,084.08 m3/y Max: 7,954,810.38 m^3/y

Carbon dioxide - CO_2
Sum:41,012,522.37 m^3 Avg: 1,367,084.08 m^3/y Max: 7,954,810.38 m^3/y

NMOC
Sum:196,860.11 m^3 Avg: 6,562.00 m^3/y Max: 38,183.09 m^3/y

LFG is a powerful greenhouse gas. When released in an unmanaged fashion, LFG may contribute anywhere from 2-4% of total global greenhouse gas emissions.1 When LFG is combusted, its effect as a greenhouse gas is significantly reduced. If LFG is recovered, it provides a source of energy that can be utilized for several energy-producing purposes and thereby generate revenue for the landfill.

Pure methane has a heating value of approximately 37 million joules per cubic meter (MJ/m^3) at standard temperature and pressure. Landfill gas that is 50 percent methane, for example, will have a heating value of 50 percent of that amount, or about 18.5 MJ/m^3 (http://www.epa.gov/coalbed/docs/inf001.pdf).

The amount of electricity that can be generated from the methane may be estimated using the following formula:

Electricity Generated (kWh) = [Gas Recovered (m^3) x Heating Value of the Gas (MJ/m^3)] / Generator Heat Rate (MJ/kWh)

The generator heat rate varies somewhat among generation technologies, but can be assumed to be about 11.6 MJ/kWh, which is appropriate for combustion turbines. Using these values, an example calculation of potential electricity production is as follows.

$$2{,}734{,}168 \text{ m}^3\text{/year} = 312 \text{ m}^3\text{/hour} \tag{5.19}$$

$$312 \text{ m}^3\text{/h} * 18.5 \text{ MJ/m}^3 \; / \; 11.6 \text{ MJ/kWh} = 498 \text{ kWh} \tag{5.20}$$

The LFG extraction system consists of the collection system (in the waste) and a suction system (of pumps, valves, etc.): The LFG collection system utilizes vertical wells.

For an average 10-meter-deep landfill, the investment in the collection system will range from $20,000-$40,000 per hectare. The LFG suction system consists of vacuum pumps, monitoring equipment, and control systems. The investment depends largely upon the sophistication of the monitoring and control system and upon the volume of LFG to be extracted. Investments in LFG suction systems range from $100-$450 per m^3 of LFG extraction capacity per hour. For an average 10-meter-deep landfill, the LFG suction system requires investments ranging from $10,000-$45,000 per hectare. Many developing countries may not need equipment of the highest level of sophistication, and the investment range for these countries may therefore be from $10,000-$25,000 per hectare (http://www.worldbank.org/urban/solid_wm/erm/ CWG%20folder/uwp4.pdf).

Utilization of LFG is most commonly achieved through the production of electric power. This is the most dependable and applicable method for utilization of LFG in lower- and middle-income countries. The investment in gas engines normally ranges between $850-$1,200 per kW installed, depending on the level of sophistication of the power generator (which ranges from gas-fueled engines to gas turbines). The smallest feasible engines to install generate from 250-500 kW, and represent a minimum investment of $200,000-$600,000.

Revenue from landfill gas recovery is significantly dependent on the type of energy produced. Price for selling of electric power to grid range from one country to another but will normally be in the range of 0.01 $/kWh (off peak hour) to 0.08 $/kWh (peak hour) with an average of 0.04 $/kWh (http://www.worldbank.org/urban/solid_wm/erm/ WG%20folder /uwp4.pdf).

Air injection systems;

The air injection system is comprised of air compressor and perforated HDPE pipes and vertical wells. Air injections systems are similar to the gas collections systems. Therefore, air injection systems can be retrofitted with vertical gas collections wells in the hybrid landfills simulating Reactor 2 (anaerobic to aerobic) and Reactor 4 (aerobic to anaerobic). On the other hand, in the landfill area simulating Reactor 3 (aerobic), air injection wells newly designed. The initial capital cost for an aerobic landfill in these cases would be similar to the costs for gas collections wells in the landfill area simulating Reactor 1.

Air compressor typically are used to force air into the waste mass through a network of perforated wells that have been installed in the landfill. Weather et al., (2001) determined that additional power required to inject air into an aerobic bioreactor was 12 times higher than the power required to extract LFG from an anaerobic bioreactor. Powell and Townsend, (2004) estimated blower capital costs from the New River Regional Landfill (NRRL) in North Central Florida. The power costs for operating the anaerobic and aerobic bioreactor scenario were estimated based on predicted blower horsepower (kW) requirements and electricity costs. The calculations indicated that the 1500 standard cubic feet per minute (scfm) anaerobic gas extractor was assumed to cost $50,000 while the 750 scfm positive displacement air injector was assumed to cost $125,000. Therefore blowers used to inject air was 5 times more expensive than LFG suction systems.

Closure and Post-Closure Care Costs;

Because so few of the facilities surveyed include closure and post-closure costs in their budgets, the Department calculated an average closure cost for each population category using engineers' closure cost estimates and actual data from landfills that had completed closure. This average closure cost is $95,000 per acre ($ 234,568 per hectar). A recent study conducted by the University of Ohio found that mean cost of closing a sanitary landfill (in Ohio) was $ 67,112 per acre ($ 165,708 per hectar) (Read et al., 2001a). Post closure cost include groundwater, surface water, leachate and landfill gas monitoring as well as maintenance of landfill cover.

Typical average aftercare (post-closure care) costs were $ 2000 ha/y for groundwater monitoring $ 750 ha /y for landfill gas monitoring $ 750 ha /y for leachate monitoring, $ 600 ha/y for surface water monitoring and $ 10,000 ha/y for landfill cover and vegetation maintenance (http://www.mfe.govt.nz/publications/waste/landfill-full-cost-accounting-guide-mar04/html/table-b6.html). Post closure costs do not include leachate, landfill gas and aeration management systems. These costs were given in operational and maintenance cost.

Landfill Management scenarios evaluated for an economic comparison are classifed herein according to reactor operations.

Alternative 1: Anaerobic Bioreactor System; with 25 Years of Liability After Closure

In this alternative, the landfill will be operated under anaerobic conditions and leachate generated at the site is collected through a drainage network at the bottom of the landfill, contained in storage tanks and then pumped into the landfill. The recirculation operation is performed for a 30-year duration (i.e.,5 years during filling operation and 25 years after landfill closure). It is assumed that the collected leachate will stabilize in a ten-year period of recirculation operations (ie., five years after closure) according to gas production potential. Therefore, after stabilization no further treatment is required prior to its final disposal. Disposal cost is assumed at $1 per thousand gallons of leachate ($ 0.26 /m^3)

Leachate Management

Leachate Production= 5 year *26,500 m^3/year + 25 year *20,700 m^3/year= 650,000 m^3
%5 leachate volume loss for Reactor 1
Leachate Recirculation Cost = 617 000 m^3* $ 2.65/ m^3= $ 1,635,050
Leachate Treatment Cost = 224,000m^3*$ 48/ m^3= $ 10,752,000 (treatment and disposal)
Leachate Disposal Cost = 393,000 m^3*$ 0.26 /m^3=$ 102,180

Gas Management

Construction costs; LFG extraction system (LFG collection and suction system) + LFG utilization system = $20,000/ha*10ha+$10,000/ha*10ha+ $850/kW*498kW=$ 722,450

Operation and maintenance costs;
Operation and maintenance costs may be estimated as 10% of investments, with an increment of 8.75 % (http://www.tcmb.gov.tr/) per year for the next 30 years= $ 9,399,682

Reveneu from gas recovery
0.04 US$/kWh$_e$ * 497kWh*24h/d*365d/yr*30 yr= $5,224,464

Closure and post-closure cost

($ 165,708 /ha*10 +[$ 2000 ha/y*10ha*25 +$ 750 ha/y*10ha*25 +$ 750 ha/y*10ha*25 +$ 600 ha/y*10ha*25 +$ 10000 ha/y*10ha*25] =$ 1,657,080 + $ 500,000 + $ 187,500 + 187,500 + $ 150,000 + $ 2,500,000 = $ 5,182,000

Alternative 2: Anaerobic-Aerobic Bioreactor System; with 25 Years of Liability After Closure

In this alternative, the landfill will be initially operated under anaerobic conditions between 2005 and 2025 for 20 years and then aerobic conditions for 10 years. Leachate generated at the site is collected through a drainage network at the bottom of the landfill, contained in storage tanks and then pumped into the landfill. The recirculation operation is performed for a 30-year duration (i.e.,5 years during filling operation and 25 years after landfill closure). It is assumed that the collected leachate will stabilize in a ten-year period of recirculation operations (ie., five years after closure) according to gas production potential. Therefore, after stabilization no further treatment is required prior to its final disposal.

Leachate Management

Leachate Production= 5 year *26,500 m^3/year + 25 year *20,700 m^3/year= 650,000 m^3
%4 leachate volume loss for Reactor 2
Leachate Recirculation Cost = 624 000 m^3* $ 2.65/ m^3= $ 1,635,600
Leachate Treatment Cost = 226,560m^3*$ 48/ m^3= $ 10,874,880 (treatment and disposal)
Leachate Disposal Cost = 397,440 m^3*$ 0.26 /m^3=$ 103,334

Gas Management

Construction costs; LFG extraction (collection and suction) system + LFG utilization system = $20,000/ha*10ha+$10,000/ha*10ha+ $850/kW*498kW=$ 722,450

Operation and maintenance costs;
operation and maintenance costs may be estimated as 10% of investments, with an increment of 8.75 % per year for the next 20 years= $ 3,593,964

Reveneu from gas recovery
0.04 US$/kWh$_e$ * 497kWh*24h/d*365d/yr*20 yr= $ 3,482,976

Aeration

Construction cost; Air pump = ($10,000/ha*10ha)*5=$ 500,000

Operation and maintenance costs;
operation and maintenance costs may be estimated as 10% of investments, with an increment of 8.75 % per year for the next 10 years= $ 750,642

Closure and post-closure cost

($ 165,708 /ha*10 +[$ 2000 ha/y*10ha*25 +$ 750 ha/y*10ha*25 +$ 750 ha/y*10ha*25 +$ 600 ha/y*10ha*25 +$ 10000 ha/y*10ha*25] =$ 1,657,080 + $ 500,000 + $ 187,500 + $ 187,500 + $150,000 + $ 2,500,000 = $ 5,182,000

Alternative 3: Aerobic Bioreactor System; with 10 Years of Liability After Closure

In this alternative, the landfill will be operated under aerobic conditions for 15 years and leachate generated at the site is collected through a drainage network at the bottom of the landfill, contained in storage tanks and then pumped into the landfill. The recirculation operation is performed for a 15-year duration (i.e.,5 years during filling operation and 10 years after landfill closure). It is assumed that the collected leachate will stabilize in a ten-year period of recirculation operations (ie., five years after closure).

Therefore, after stabilization no further treatment is required prior to its final disposal. Moreover, economic analysis was done for 30 years operation.

Leachate Management

15 years

Leachate Production= 5 year *26,500 m^3/year + 10 year *20,700 m^3/year= 339,500 m^3
%34 leachate volume loss for Reactor 3
Leachate Recirculation Cost = 224,070 m^3* $ 2.65/ m^3= $ 593,786
Leachate Treatment Cost = 155,760 m^3*$ 48/ m^3= $ 7,476,480 (treatment and disposal)
Leachate Disposal Cost = 68,310 m^3*$ 0.26 /m^3=$ 17,761

30 years

Leachate Production= 5 year *26,500 m^3/year + 25 year *20,700 m3/year= 650,000 m^3
%34 leachate volume loss for Reactor 3
Leachate Recirculation Cost = 429,000 m^3* $ 2.65/ m^3= $ 1,136,850
Leachate Treatment Cost = 155,760m^3*$ 48/ m^3= $ 7,476,480 (treatment and disposal)
Leachate Disposal Cost = 273,240 m^3*$ 0.26 /m^3=$ 71,042

Aeration

15 years

Construction costs; collection system +aeration system
=$20,000/ha*10ha+($10,000/ha*10ha)*5=$ 700,000

Operation and maintenance costs; operation and maintenance costs may be estimated as 10% of investments, with an increment of 8.75 % per year for the next 15 years= $ 2,015,328

30 years

Construction costs; collection system +aeration system =$20,000/ha*10ha+($10,000/ha*10ha)*5=$ 700,000

Operation and maintenance costs; operation and maintenance costs may be estimated as 10% of investments, with an increment of 8.75 % per year for the next 30 years= $ 9,107,588

Closure and post-closure cost

15 years

($ 165,708 /ha*10 +[$ 2000 ha/y*10ha*10 +$ 750 ha/y*10ha*10 +$ 750 ha/y*10ha*10 +$ 600 ha/y*10ha*10 +$ 10000 ha/y*10ha*10] =$ 1,657,080 + $ 200,000 + $ 75,000 + $ 75,000 + $ 60,000 + $ 1,000,000 = $ 3,067,080

30 years

($ 165,708 /ha*10 +[$ 2000 ha/y*10ha*25 +$ 750 ha/y*10ha*25 +$ 750 ha/y*10ha*25 +$ 600 ha/y*10ha*25 +$ 10000 ha/y*10ha*25] =$ 1,657,080 + $ 500,000 + $ 187,500 + $ 187,500 + $ 150,000 + $ 2,500,000 = $ 5,182,000

Alternative 4: Aerobic-Anaerobic Bioreactor System; with 25 Years of Liability After Closure

In this alternative, the landfill will initially be operated under aerobic conditions for 5 years and then anaerobic conditions for 25 years. Leachate generated at the site is collected through a drainage network at the bottom of the landfill, contained in storage tanks and then pumped into the landfill. The recirculation operation is performed for a 30-year duration (i.e.,5 years during filling operation and 25 years after landfill closure). It is assumed that the collected leachate will stabilize in a ten-year period of recirculation operations (ie., five years after closure).

Leachate Management

Leachate Production= 5 year *26,500 m^3/year + 25 year *20,700 m^3/year= 650,000 m^3
%30 leachate volume loss for Reactor 4
Leachate Recirculation Cost = 455 000 m^3* \$ 2.65/ m^3= \$ 1,205,750
Leachate Treatment Cost = 165,200m^3*\$ 48/ m^3= \$ 7,929,600 (treatment and disposal)
Leachate Disposal Cost = 289,800 m^3*\$ 0.26 /m^3=\$ 75,348

Gas Management

Construction costs; LFG extraction (collection and suction) system + LFG utilization system = \$20,000/ha*10ha+\$10,000/ha*10ha+ \$850/kW*498kW=\$ 722,450

Operation and maintenance costs; operation and maintenance costs may be estimated as 10% of investments, with an increment of 8.75 % per year for the next 25 years= \$ 5,896,858

Reveneu from gas recovery
0.04 US\$/kWh$_e$ * 497kWh*24h/d*365d/yr*25 yr= \$ 4,353,720

Aeration

Construction costs; Air pump = (\$10,000/ha*10ha)*5=\$ 500,000

Operation and maintenance costs; operation and maintenance costs may be estimated as 10% of investments, with an increment of 8.75 % per year for 5 years= \$ 297,749

Closure and post-closure cost

(\$ 165,708 /ha*10 +[\$ 2000 ha/y*10ha*25 +\$ 750 ha/y*10ha*25 +\$ 750 ha/y*10ha*25 +\$ 600 ha/y*10ha*25 +\$ 10000 ha/y*10ha*25] =\$ 1,657,080 + \$ 500,000 + \$ 187,500 + \$ 187,500 + \$ 150,000 + \$ 2,500,000 = \$ 5,182,000

Table 5.18 . Comparison of bioreactor landfill costs

		Alternative 1	Alternative 2	Alternative 3 15 years	Alternative 3 30 years	Alternative 4
Leachate Management (Capital, O&M cost)		$ 12,489,230	$ 12,613,814	$ 8,088,027	$ 8,684,372	$ 9,210,698
Capital Cost	Gas Management	$ 722,450	$ 722,450			$ 722,450
	Aeration		$ 500,000	$ 700,000	$ 700,000	$ 500,000
Operational Cost		$ 9,399,682	$ 4,344,606	$ 2,015,328	$ 9,107,588	$ 6,194,600
Closure and Post-Closure Cost		$ 5,182,000	$ 5,182,000	$ 3,067,080	$ 5,182,000	$ 5,182,000
	Total	$ 27,793,362	$ 22,862,870	$ 13,870,435	$ 23,673,960	$ 21,809,748
	Reveneu	$ 5,224,464	$ 3,482,976			$ 4,353,720
	Overall Total	$ 22,568,898	$ 19,379,894	$ 13,870,435	$ 23,673,960	$ 17,456,028

It is clear from Table 5.18 that alternative 3 (aerobic landfill) option is economically favorable by comprasion to other management scenarios of bioreactor landfilling. The cost estimated for leachate management at this particular landfill was $ 8,088,027 (Alternative 3). This management cost is less than about 35% of Alternative 1 , 36% of Alternative 2 and 12% of Alternative 4 since leachate volume reduction due to the aeration caused decreasing of leachate management cost. Besides, operational costs and closure and post closure costs of aerobic landfill are less than the other alternatives because aerobic landfill (Alternative 3) offered the potential to achieve the same stabilization in fifteen years that landfills require 30 years or longer to reach. If aerobic landfill operated for 30 years, operation cost would be $ 9,107,588 as similar to Alternative 1. To sum up, Alternative 3 for 15 years is the cheapest landfill method within landfill management alternatives. Costs of Alternative 4 and Alternative 2 follow aerobic landfill (Alternative 3), respectively. Both aeration and gas management systems increase the total cost of these landfills. Alternative 3 for a 30 year-operation and Alternative 1 (anaerobic landfill) in spite of its highest revenue from landfill gas recovery are the most expensive options. Berge et al., (2009) also described an economical model developed to evaluate the impact of various operational (anaerobic, aerobic and hybrid) and construction (retrofit and as-built) bioreactor landfill strategies on project economics and confirmed that both the as built and aerobic bioreactor landfills have lower costs than the retrofit and traditional landfills.

6. SUMMARY AND CONCLUSIONS

Concern about air and water polution emanating from landfills, coupled with limited suitable land available for the ever increasing needs of disposed of municipal solid waste (MSW), have led to landfill operations that involve significant active management of the refuse mass. Therefore, this study aimed to evaluate an efficient and cost-effective landfill management concept by using aerobic and anaerobic processes. The overall performance of the different landfill concepts was compared to better understand the potential for in-situ attenuation of carbon, nitrogen, sulfur and heavy metals under aerobic and anaerobic conditions. For this purpose, four landfill bioreactors were used in a thermo-insulated room at a constant temperature of 32 ºC to enhance the growth of microorganisms. These reactors were constructed and filled with shredded and compacted municipal solid waste having typical solid waste composition determined for İstanbul region. The bioreactors were operated under wet-tomb management strategy by using leachate recirculation. Moreover, moisture addition was made into the bioreactors in order to simulate the annual rainfall. Aerobic conditions in the reactors were developed by using an air pump. In order to evaluate and determine an efficient and cost-effective landfill management system, aerobic pretreated and aerobic remediated landfill concepts were also operated in the laboratory.

In accordance with these objectives, obtained results can be summarized as follows:

Although all reactors were acidic at the beginning of the experiment, pH values became sharply neutral after 35 days in Reactors 3 and 4 under aerobic conditions. The conversion of the Reactor 4 from aerobic to anaerobic conditions on Day 75 did not affect pH values in the system. On the other hand, pH values obtained from Reactors 1 and 2 under anaerobic conditions 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 of both reactors. After the onset of methanogenic conditions, resulting in faster volatile organic acids utilization, pH increased to 7.0 on Day 446 in Reactor 1 and on Day 146 in

Reactor 2. Due to an imbalance between fermentative and methanogenic activity and accumulation of organic acids, pH in Reactor 1 stayed at acidic values for longer time. Moreover, the conversion of Reactor 2 from anaerobic to aerobic conditions on Day 264 did not affect alkaline pH values in the system.

While ORP values in all reactors were negative due to the existence of highly reducing environment, ORP values of Reactors 3 and 4 under aerobic conditions began to be more negative throughout the first 75 days due to rapid organic degradation. Low ORP values for leachate in the aerobic reactors were caused by injection of air into the unsaturated upper zone only and accumulation of leachate at the bottom of reactors remained anaerobic. After Day 75, the ORP values for aerobic reactors reached to positive values. On the other hand, ORP values of reactors under anaerobic conditions decreased to -200 mV which is a prerequisite for the efficiency of methanogenic activity after 430 days in Reactor 1 and 140 days in Reactor 2. After addition of air into Reactor 2, ORP values, firstly decreased to lower values due to ongoing degradation of waste and accumulation in leachate and then increased to positive values at the end of study.

Conductivity and salinity of leachate showed same decreasing trend in all reactors because of washout and immobilization of ions. Reductions of conductivity and salinity values from initial to minimum values at the end of study were calculated as 61 and 62 % for Reactor 1, 77 and 79 % for Reactor 2, 50 and 52 % for Reactor 3, 50 and 49 % for Reactor 4, respectively. Together with the conversion of the reactors to opposite conditions, conductivity and salinity reductions were calculated as 9 and 9% for Reactor 2 on Day 264 and 11 and 12 % for Reactor 4 on Day 77, respectively.

High initial leachate color values for Reactors 1,2,3 & 4 were removed by 86 %, 93 %, 86 % and 85 %, respectively at the end of study. The color of leachate changed sequentially from gray to dark gray, and then black, brown and pale yellow towards the end of study because of in-situ attenuation mechanisms in the reactors. Color removal was 71 % for Reactor 2 on Day 264 and 53% for Reactor 4 on Day 77. The highest removal was observed in Reactor 2. Similarly, turbidity removal of Reactors 1,2,3&4 were 88 %, 99 %, 100 % and 99 %, respectively. Turbidity removal was 97 % for Reactor 2 on Day 264 and 68 % for Reactor 4 on Day 77. Conversion of Reactor 2 from anaerobic to aerobic conditions did not make so much difference for turbidity removal due to the rapid conversion of organic acids to methane and nearly completed organic degradation under anaerobic conditions.

The COD concentrations obtained from all reactors have firstly shown an increase due to rapid relase and hydrolysis of complex organics from solid waste to leachate. Aeration enabled significantly faster biodegradation of organic matter in Reactors 3 and 4. A considerable reduction of leachate COD was observed during approximately 75 days of aeration. COD concentrations reached their nearly constant values due to completion of waste stabilization in the reactor. COD removals were 96% for Reactor 3 on Day 374 and 90 % for Reactor 4 on Day 77 and 97% on Day 374. On the other hand, COD concentrations in Reactors 1 and 2 under anaerobic conditions remained at same high levels due to the accumulation of organic acids that was confirmed with slight decrease in pH values and increase in VFA concentrations. Sharp decreases in COD were observed after Day 135 in Reactor 2 and after Day 433 in Reactor 1 due to the utilization of volatile organic acids and decrease of organic content reached maximum, stabilizing the organic content of the waste matrix. Together with air addition on Day 264, COD concentrations of Reactor 2 decreased slightly to about 400 mg/L. Most of readily biodegradable organics were stabilized during anaerobic degradation process and then aeration helped to nearly complete the conversion of waste. COD removals were 99 % for Reactor 1 on Day 630 and 97 % and 99 % for Reactor 2 on Day 264 and 630, respectively. TOC and BOD_5 exhibited a similar trend with COD removal. Degradation of organic carbon (TOC) was accomplished at 99 % in Reactor 1 and 2, 90 % in Reactor 3 and 93 % in Reactor 4 at the end of experiment. During conversion of degradation conditions, TOC removal was 97 % on Day 264 for Reactor 2 and 84 % on Day 77 for Reactor 4. Similarly BOD_5 was removed at 100 % in all reactors at the end of experiments due to the high rate of BOD_5 utilization by aerobic and anaerobic microorganisms.

The intensity of the TVFA generated from Reactors 3 and 4 was insignificant due to rapid degradation of organics at the beginning when compared to the TVFA generated from Reactors 1 and 2 under anaerobic conditions. The predominant species of volatile fatty acids detected in Reactors 1 and 2 were butyric, caproic and acetic acids, accounting for approximately 70 % of the total volatile acids.

While organic compounds in leachate decrease due to degradation and washout, inorganic materials decreased due to washout, filtration, precipitation and/or sorption within the landfill mass. During the experimental period, TS and TVS concentrations of leachate decreased similar to COD concentrations. Removals of TS were 94 % for Reactor 1 and 93 % for Reactor 2 on Day 630 and 56 % for Reactor 3 and 60 % for Reactor 4 on Day 374. While TS removal was only 21 % for Reactor 4 on Day 77 as it was converted from aerobic to anaerobic conditions, TS was almost removed in Reactor 2 during anaerobic degradation and it was 85 % on Day 264 as it was converted from anaerobic to aerobic conditions. Similarly, removals of TVS were 97 % for Reactor 1 and 98 % for Reactor 2 on Day 630 and 74% for Reactor 3 and 75 % for Reactor 4 on Day 374.

Leachate TKN and NH_3-N concentrations in Reactors 1 and 2 accumulated to a high level since there is no ammonia elimination process under anaerobic conditions. TKN and NH_3-N were removed as 48 % and 38 % for Reactor 1 until the end of study and just only 4 % and 2 % for Reactor 2 until the turning point on Day 264. After the operational conditions in Reactor 2 became aerobic, TKN and NH_3-N removals increased to 90 % and 92 % at the end. TKN and NH_3-N concentrations in Reactor 3 under aerobic conditions decreased to their lowest values when compared to the other reactors and were removed as 94 % and 99 %, respectively on Day 374. TKN and NH_3-N removals of Reactor 4 were influenced in a negative way due to the conversion of the reactor from aerobic to anaerobic conditions and were calculated as 37 % and 64 % at the end of the experiment. Therefore, aerobic landfill bioreactor with leachate recirculation could effectively remove ammonia-nitrogen and since the concentrations of nitrogen are reduced, the need for ex-situ leachate treatment could also be reduced, depending on applicable regulations. Decomposition of organic material containing phosphorus resulted in decrease in the leachate orthophosphate concentrations in all reactors. Phosphorus attenuation was attributed to microbial utilization, washout (dilution) and possible complexation reactions. To sum up, reductions of total phosphorus and orthophosphate were 91 % and 94 % for Reactor 1, 95 % and 96 % for Reactor 2, 83 % and 95 % for Reactor 3 and 72 % and 80 % for Reactor 4 at the end of experiments.

Alkalinity concentrations in all reactors throughout the experimental study were 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 reactors under aerobic conditions was the result of oxidation of ammonia to nitrate and washout in the system, decrease in the alkalinity from the reactors under anaerobic conditions corresponds to the decrease in the organic content of the waste, and therefore the decrease of volatile organic acids. On the other hand, acidity in anaerobic reactors were high due to organic acids whereas acidity in aerobic reactors were low as a result of CO_2 stripping by air.

Since highly reducing conditions, confirmed by negative ORP values, were established in the reactors under aerobic conditions, sulfate concentrations were not observed initially. While sulfate concentrations began to appear in Reactor 3 after the onset of oxidizing conditions during Day 75, sulfate concentrations of Reactor 4 were not measured throughout the experiment due to the conversion from aerobic to anaerobic conditions. On the other hand, sulfates in the reactors under anaerobic conditions are reduced to sulfides as the system progresses from acidogenic to methanogenic. Together with air additon into Reactor 2, sulfate that was reduced initially to sulfide began oxidizing back to sulfate. However, this started not just after aeration but 218 days of aeration. On the other hand, sulfide concentrations were generally not observed in the reactors because formed sulfides combining with heavy metals precipitated immediately and did not remain in the free form. Sulfide concentrations were observed in Reactor 3 at the end of experiment due to the oxidation of sulfide to sulfate and free sulfide ions as a result of the presence of other ions including carbonate, phosphate and observed in Reactor 1 between Days 316 and 480 due to the rapid degredation and sharp decrease in high sulfate concentrations.

Chloride was monitored as a tracer to estimate the effect of dilution. A decrease in chloride concentrations in the reactors proved the existence of washout. Chloride reductions or Reactors 1,2,3, 4 were 78%, 74%, 50 % and 63%, respectively.

Alkali and alkaline earth metals (Na, K, Mg and Ca) and heavy metal concentrations (Fe, Mn, Cu, Cd, Ni, Zn, Cr and Pb) obtained from the reactors have shown the similar decreasing trend during the experimental study as a result of precipitation. Metal solubility in the leachates under anaerobic conditions is initially controlled by the availability of sulfides. When sulfides became unavailable then heavy metals are controlled by other ions such as sulfate, carbonate and phosphate. After the establishment of reducing environment, sulfate reduced to sulfide and all heavy metals precipitated with sulfides. On the other hand, because highly reducing environment was established in the reactor under aerobic conditions as soon as waste was loaded to the reactors, heavy metals in the reactors precipitated with sulfides. Therefore, no significant release of heavy metals under aerobic conditions was observed compared to anaerobic bioreactors.

Gas production and its composition monitored during the study period supported the findings from the leachate analysis. Initial gas production in Reactor 1 started on Day 58, steady daily gas production was measured around Day 330 and reached to 20 L/day on Day 445 which was the highest value of gas production. In Reactor 2 (anaerobic-aerobic) gas production was observed on Day 92 and reached its peak values between Days 148 and 200. The highest volume of gas produced was 17.7 L/day on Day 151. In Reactor 4 (aerobically pretreated), gas production started after reactor was closed on Day 75 and did not exceed 2 L/day due to nearly completed stabilization of readily degradable organic carbon sources. Reactor 1 exhibited some retardation of gas production because acidic conditions resulting from rapid degradation, and accumulation of VFAs inhibited gas generation. This retardation was also confirmed by gas composition of the reactor. Methane concentrations began to appear by Day 145 and reached to 50 % by composition around Day 400. In Reactor 2, methane percentage reached to about 50 % on Day 135 and declined to 19.5 % on Day 265 after air addition and was observed until Day 320. After this day, methane was not detected in the reactor. Gas composition of Reactor 3 (aerobic) was 4.95% CO_2, 14.41% O_2 and 80.64% N_2 at the end of the experiment. In Reactor 4, at first gas composition was similar to Reactor 3 and then, methane generation was observed after the onset of anaerobic conditions. Methane generation reached rapidly to about 50% by composition for a short period and slowly decreased due to termination of the nutrients and organics during aerobic conditions. This is evidenced by slow waste utilization, reflected through low volume of gas produced and low methane concentration. Moreover, cumulative gas productions of Reactor 1, 2 and 4 were found as 1497 L, 753 L and 63 L, respectively.

Settlement of waste is important due to its potential to allow disposal of more waste in the landfills. Settlements of Reactors 1, 2, 3 and 4 were measured as 4 cm, 9 cm, 32 cm and 31 cm, respectively. Based on these measurements, higher degree of settlement was achieved in the reactors under aerobic degradation.

Overall economic analysis results demonstrated that aerobic decomposition of MSW provides cost-effective landfill technology. In aerobic landfills, long-term liability and cost associcated with landfill operation and closure will be greatly reduced. Aerobic remediation and aerobic pretreated solutions for landfills are also cost-effective when compared to anaerobic landfill costs. On the other hand, although landfill gas for energy recovery is feasible, the methane management approach of anaerobic landfill does not offer attractive economic advantages when compared to other landfill options.

Based upon experimental results obtained during the investigation, the following conclusions are reached.

1. The anaerobic bioreactor landfill shows the highest levels of all pollutional parameters, with high concentrations of COD, TOC, BOD, ammonia, phosphorus, sulfate and metals in the leachate. Biogas production was delayed by the initial acid phase of waste biodegradation.
2. Aeration of the waste mass provides rapid oxidation of organics and nitrogen when compared to the anaerobic bioreactor landfill. More than 90% of COD was decomposed within 70 days in the aerobic bioreactor compared to 462 days in the anaerobic bioreactor.
3. Aerobic pretreated and aerobic remediated bioreactor landfill concepts were also more efficient in terms of waste stabilization and leachate treatment when compared to the anaerobic bioreactor. COD, TOC, ammonia, sulfate removals of these landfill concepts are more than anaerobic landfill concept due to the treatment of waste with air. On the other hand, biogas production from aerobically pretreated bioreactor landfill was not efficient for energy utilization.
4. Although the organic strength of leachate is reduced in bioreactor landfills, recirculating the leachate increased the rate of ammonification and resulted in

accumulation of higher levels of ammonia-nitrogen concentrations in anaerobic bioreactors compared to the bioreactors under aerobic conditions. Ammonia concentrations in aerobic reactor decreased to 5 mg/L at the end of experiments, their concentrations in anaerobic reactor reached to about 660 mg/L. In aerobically pretreated and remediated bioreactors, ammonia concentrations were measured as 277 and 123 mg/L at the end of experiment.

5. Heavy metal concentrations are low in the aerobic reactors compared to anaerobic reactors because solid wastes stabilize rapidly in the landfills under aerobic conditions and the pH reaches to neutral values earlier. Heavy metal inhibition is considered to be the most important factor causing delays in the release and conversion of organic pollutants in landfills. Analysis of data indicated that organic fraction of waste continued to decrease since the range of metal concentrations were fairly low to inhibit the microorganisms.
6. The reactors were designed and operated to simulate landfill environment as an controlled anaerobic and/or aerobic bioreactors with leachate recirculation, providing accelerated stabilization of the waste matrix and in-situ leachate treatment by reintroduction of necessary nutrients for microorganism growth. Moreover, leachate recirculation did not allow the reactors under aerobic conditions to rise elevated temperatures causing fires in landfills. Waste mass temperatures and moisture are maintained within optimal ranges by reason of leachate recirculation.
7. Aeration decreased leachate volume in the reactors. Reductions are calculated from water balance as 5% for Reactor 1, 4% for Reactor 2, 34% for Reactor 3, 30% for Reactor 4. The reduction in leachate volume will decrease the need and cost of off-site treatment.
8. The waste settlement in the aerobic reactors occurred faster than the waste settlement in the anaerobic reactors. Higher degree of settlement was achieved in the aerobic bioreactor where settlement was about 37% at 374 days. Anaerobic bioreactor exhibited settlement about 5% after 630 days.
9. Comparing the anaerobic and aerobic reactors, the aerobic reactor was more effective in terms of COD reduction and waste stabilization. While aerobic reactor was completed within 374 days, anaerobic reactor was operated for 630 days.

10. Economic analysis indicated that the aerobic landfill approach provides potentially significant saving for landfills when it was compared with the costs of methane gas and leachate management, closure and post-closure and the risk associated with anaerobic landfill operations.

Overall, the results of this study showed that aeration in municipal solid waste landfills is a viable management option for the accelerated stabilization of a waste matrix. Aeration is a feasible way to treat the leachate *in situ*, and, therefore, decrease the cost of further external treatment. Combination of different operational conditions may be the best to achieve the optimum waste stabilization. Aerobic pretreated and aerobic remediated landfill concepts aim to get feasible energy by enhancement of methane generation and reduce possible adverse effects of conventional landfills. Therefore these concepts provide safe disposal of waste when compared to anaerobic landfills. On the other hand, although anaerobic landfills were not efficient and not cost effective due to post-closure monitoring and off-site leachate treatment, anaerobic landfills are expected to reduce cost because of energy recovery. Sustainable landfill management is also subjected to government regulations. Therefore, final decision must be made not only on the basis of technical feasibility and economic viability, but on legislative procedures and permitting sytems as well.

To sum up, it may not prove surprising that waste can rapidly decompose in aerobic conditions. It could be also anticipated that methane concentrations decreased as a result of air addition. However, in addition to these common consequences, the results of this study, which could possibly occur in large scale landfill, may be helpful for landfill operators and engineers when choosing aerobic and anaerobic systems These results can be used to compare aerobic and anaerobic landfills for life-cycle assessment. Aerobic landfills are expected to reduce the cost for monitoring and leachate treatment due to rapid waste decomposition and low organic carbon.

Recommendations

In Reactor 4, aeration accelerated waste degradation rapidly and after conversion of the reactor from aerobic to anaerobic conditions, gas generation was measured lesser than expected gas generation. Further research is required to optimize aeration ratio for pretreatment of MSW

For aeration to be undertaken willingly by operators, it needs to be economically attractive, and the savings in aftercare costs can be contribute to this attractiveness. Further research is required to optimize cost-effective aeration ratio.

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