IN SITU IMMOBILIZATION OF THE SELECTED HEAVY METALS BY SULFIDE COMPOUNDS IN LANDFILLS UNDER METHANOGENETIC CONDITONS

by

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Keywords: landfill, solid waste, co-disposal, leachate recirculation, heavy metals, sulfides

Co-disposal is a technique for the controlled disposal of hazardous wastes together with municipal solid waste. Co-disposal of industrial wastes including heavy metals and disposal of household hazardous substances such as batteries, paints, dyes and inks in paper result in release of heavy metals into a landfill environment. Zinc, iron, nickel, copper and cadmium are the most common heavy metals disposed to landfills. These metals are controlled by several attenuation mechanisms including adsorption, acid-base, oxidation-reduction and precipitation-complexation reactions.

This research aimed to better understand the extent of heavy metal attenuation in landfills by means of precipitation by sulfide compounds. The effect of selected heavy metals (Zn, Cu, Cd, Fe, Ni) on solid waste stabilization together with the effect of leachate recirculation on the attenuation mechanisms was also investigated. For this purpose, two landfill simulating reactors were used in the laboratory. These reactors were constructed and filled with shredded and compacted municipal solid waste having typical solid waste composition determined for İstanbul region. Two reactors, one with leachate recirculation, the other without were operated in the constant temperature room of 32 °C to enhance the growth of anaerobic microorganisms. Moreover, moisture addition was done into the reactors in order to simulate the annual rainfall. After the onset of the methanogenetic conditions in both reactors, the selected heavy metals including iron, copper, nickel, cadmium and zinc were added into the simulated landfill reactors. The metals (Fe, Cu, Ni, Cd, Zn) were prepared by dissolving the metal salts in one liter deionized water and introduced into the bioreactors according to the amounts suggested for co-disposal under the directives of the Turkish Hazardous Waste Control Regulations to prevent inhibition of the microbially mediated processes during waste stabilization

This research indicated that when sulfide concentration was very low or insufficient, the removal of the metals was controlled by other anions such as $CO_3^{=}$ and PO_4^{-3} until the reduction of sulfate coming from loaded metal salts into the reactors Moreover, leachate recirculation offers opportunities for more rapid waste stabilization including attenuation of co-disposed heavy metals.

METHANOGENİC ŞARTLAR ALTINDA DÜZENLİ DEPOLAMA SAHALARINDA AĞIR METALLERİN SÜLFÜR BİLEŞİKLERİ İLE GİDERİLMESİ

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Anahtar kelimeler: depolama alanı, katı atık, birlikte bertaraf etme, sızıntı suyunun geriye devri, ağır metaller, sülfürler

Birlikte bertaraf etme, evsel katı atıklarla tehlikeli atıkların kontrollü bir şekilde birlikte uzaklaştırılması yönetimidir. Ağır metal içeren sanayii atıkları ile evlerden kaynaklanan pil, boya, mürekkep gibi tehlikeli maddelerin düzenli depolama alanlarına atılması, bu alanlardaki ağır metal konsantrasyonun artışına neden olur.Çinko, demir, nikel, bakır ve kadmiyum ise depolama alanlarında en çok görülen metallerdir. Adsorpsiyon, asit-baz, yükseltgenme-indirgenme, çöktürme-kompleks oluşturma gibi reaksiyonlar ağır metallerin giderilmesini kontrol eden mekanizmalardan birkaçıdır.

Depolama sahalarına gelen ağır metallerin sülfürlerle çöktürülmesi bu çalışmanın esas amacıdır. Sızıntı suyunun geri devrinin metal giderimine etkisi de ikinci bir amaç olarak incelendi. Bu nedenle laboratuar şartlarında düzenli depolama alanlarını simule eden iki reaktör işletildi. Bu reaktörler İstanbul'un çöp özelliklerine sahip, sıkıştırılmış ve ufaltılmış çöple dolduruldu. Biri geri devirli, diğeri geri devirsiz olan bu iki reaktör anaerobik microorganizmaların gelişimini arttırmak için 32 °C sabit sıcaklıktaki özel odada işletildi. Ayrıca İstanbul bölgesindeki yağışa eşit miktarda düzenli olarak yağmur suyu eklendi. Methanogenic ortam iki reaktörde de kurulduktan sonra, demir,bakır, nikel, çinko ve

kadmiyum reaktörlere yüklendi. Bu metaller Türk Tehlikeli Atık Yönetmeliğinde verilen değerlere göre reaktörlere dozlandı.

Araştırmanın sonucuna göre, ortamda yeterli miktarda sülfür olmaması halinde metaller sülfat sülfide indirgenene kadar, $CO_3^{=}$ ve PO_4^{-3} gibi diğer anyonlarla çöker. Ayrıca sızıntı suyunun geri devri daha hızlı katı atık stabilizasyonu ve daha çabuk metal giderimi sağlar.

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1. INTRODUCTION

The amount and types of both municipal and industrial solid wastes have increased gradually because of economical and technological developments. Effective management of increasing amounts of these solid wastes has become a major social and environmental concern. Although there are many methods such as incineration, waste minimization, waste recovery and recycling to reduce the volume of the solid wastes, landfilling is the ultimate disposal method for wastes that can not be recovered. Moreover, landfilling is comparatively simple and economic way for solid waste disposal. In most countries, municipal solid waste and hazardous waste which are generated from commercial and industrial areas are disposed into sanitary and secure landfills, respectively. Secure landfills for disposal of hazardous materials are expensive and their operation requires intensive care. Co-disposal is a technique for the controlled disposal of hazardous wastes together with municipal solid waste. Therefore, co-disposal is an important management strategy to decrease the total cost of waste disposal in developing countries.

Two management systems for sanitary landfills, conventional waste management and bioreactor landfill operation, have been developed to eliminate the potential environmental risk of leachate and gas production. Although conventional landfills consist of cells and lifts with liners, drains, gas vents, leak detection systems and intermediate and final covers, the inadequacy of conventional waste management caused the evaluation of bioreactor landfills having leachate recirculation management strategy. During the leachate recirculation, leachate is collected, stored and reinjected back into the landfill to promote *in situ* anaerobic biological treatment. Therefore, bioreactor landfills provide rapid, complete attenuation of solid waste constituents.

Heavy metals reach the sanitary landfill by the co-disposal of industrial wastes, incineration ashes, mine wastes. Moreover, municipal solid waste may include many household hazardous substances. Batteries, paints, dyes, and inks in paper, pesticides and fertilizers in yard waste are examples of some of the hazardous substances disposed to landfills by these sources. Therefore, a release of heavy metals into a landfill environment is expected with co-disposal of industrial wastes and disposal of household hazardous substances. Zinc, iron, nickel, copper and cadmium are the most common heavy metals disposed to landfills.

Co-disposal aims to reduce potential toxic effect of heavy metals by *in situ* attenuation mechanisms present inside landfills. There are several factors for the control of metal solubility in landfills including the concentrations of the potential precipitant species such as hydroxide, carbonate, sulfate and sulfide, the existence of complexing agents which tends to increase metal solubility, the pH-ORP relationships which will impact both heavy metal and precipitant speciation, ionic strength and washout effects. Therefore, in this research, it was aimed to better understand the extent of heavy metal attenuation in landfills by means of precipitation as sulfide compounds. With this approach, the attenuation capacity of co-disposal landfill was examined and used to describe associated attenuation mechanisms basic to the development of appropriate landfill design and operating strategies. The effect of selected heavy metals (Zn, Cu, Cd, Fe, Ni) on solid waste stabilization together with the effect of leachate recirculation on the attenuation mechanisms was also investigated.

Since low pH values in landfills in acidogenic phase cause solubilization and mobilization of heavy metals, methanogenesis and neutral pH must be established within the landfill site to form insoluble metals in the reducing atmosphere before the co-disposal commences. With this approach, two simulated landfill reactors, one with leachate recirculation, the other without were operated under different operational stages to ensure the required conditions. After the onset of the methanogenetic conditions in both reactors, the selected heavy metals including iron, copper, nickel, cadmium and zinc were added into the simulated landfill reactors to understand landfill assimilative behavior and the effect of leachate recirculation. The metals (Fe, Cu, Ni, Cd, Zn) were prepared by dissolving the metal salts in one liter deionized water and introduced into the bioreactors according to the amounts suggested for co-disposal under the directives of the Turkish Hazardous Waste Control Regulations to prevent inhibition of the microbially mediated processes during waste stabilization.

The results obtained from two reactors were compared to find the effect of leachate recycle on the removal of heavy metals in terms of precipitation by sulfide compounds. Furthermore, the effects of enhancement techniques such as buffer addition and frequency of leachate recirculation on waste degradation potential were determined.

2. LITERATURE REVIEW

The literature review has been divided into three main sections: (1) landfill stabilization and factors affecting landfill stabilization (2) management systems in sanitary landfills with a special emphasis on leachate recirculation management strategy (3) co-disposal of heavy metals and co-disposal processes.

2.1. LANDFILL STABILIZATION

2.1.1 Landfill Stabilization Processes

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). The significance and longevity of these processes are determined by climatogical conditions, operational variables and management options (Pohland *et al.*, 1993).

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 Kjeldelsen, 1989 ; Pohland, 1992). However, a four-stage process involving hydrolysis, acidogenesis, acetogenesis and methanogenesis is used widely. Figure 2.1 illustrates four stages of anaerobic decomposition.

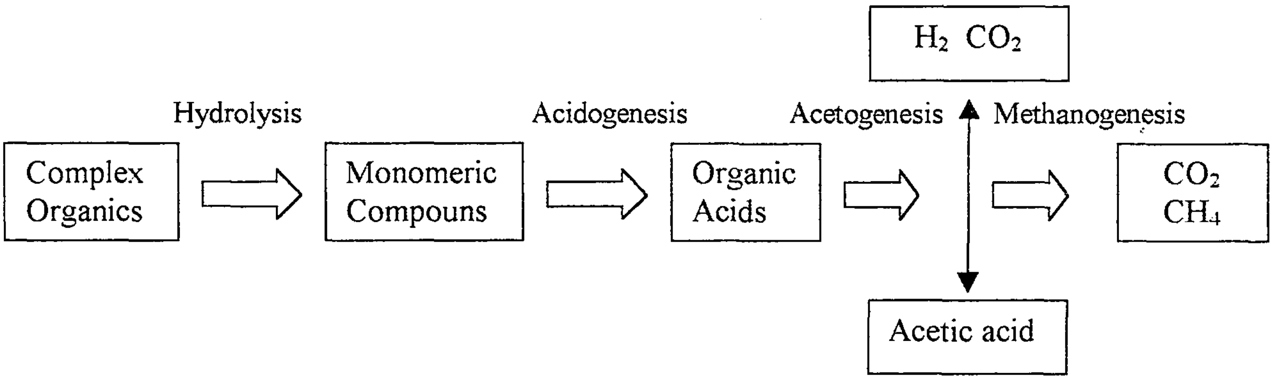


Figure 2.1 Four Stages in the Anaerobic Decomposition of Wastes (Archer and Kirsop, 1990).

In the first stage, complex organics such as cellulose, proteins, lipids and carbohydrates are hydrolyzed to dissolved organics, primarily sugars, alcohols, amino acids 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 (CH_4) and carbon dioxide (CO_2) by specific group of microorganism called as methanogenesis. 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 methonogens and a final group of bacteria that utilize formic acid and methanol to produce methane.

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

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 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 hydrolysis 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 the 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 they are used to understand intensity and longevity of each phase of landfill stabilization in leachate and gas composition. Pohland reported these indicator parameters as ; pH, oxidation-reduction potential (ORP), chemical oxygen demand (COD), five day biochemical oxygen demand (BOD_5), volatile organic acids (VOA), nitrogen, and phosphorus, alkalinity, heavy metal concentration, conductivity, chloride concentration, nitrates and sulfates, and the presence of bacteria and viruses. Gas phase can be analyzed for daily production and composition such as methane and carbon dioxide (Pohland *et al.*, 1993). The changes in the selected indicator parameters throughout the phases of the landfill stabilization are illustrated in the Figure 2.2

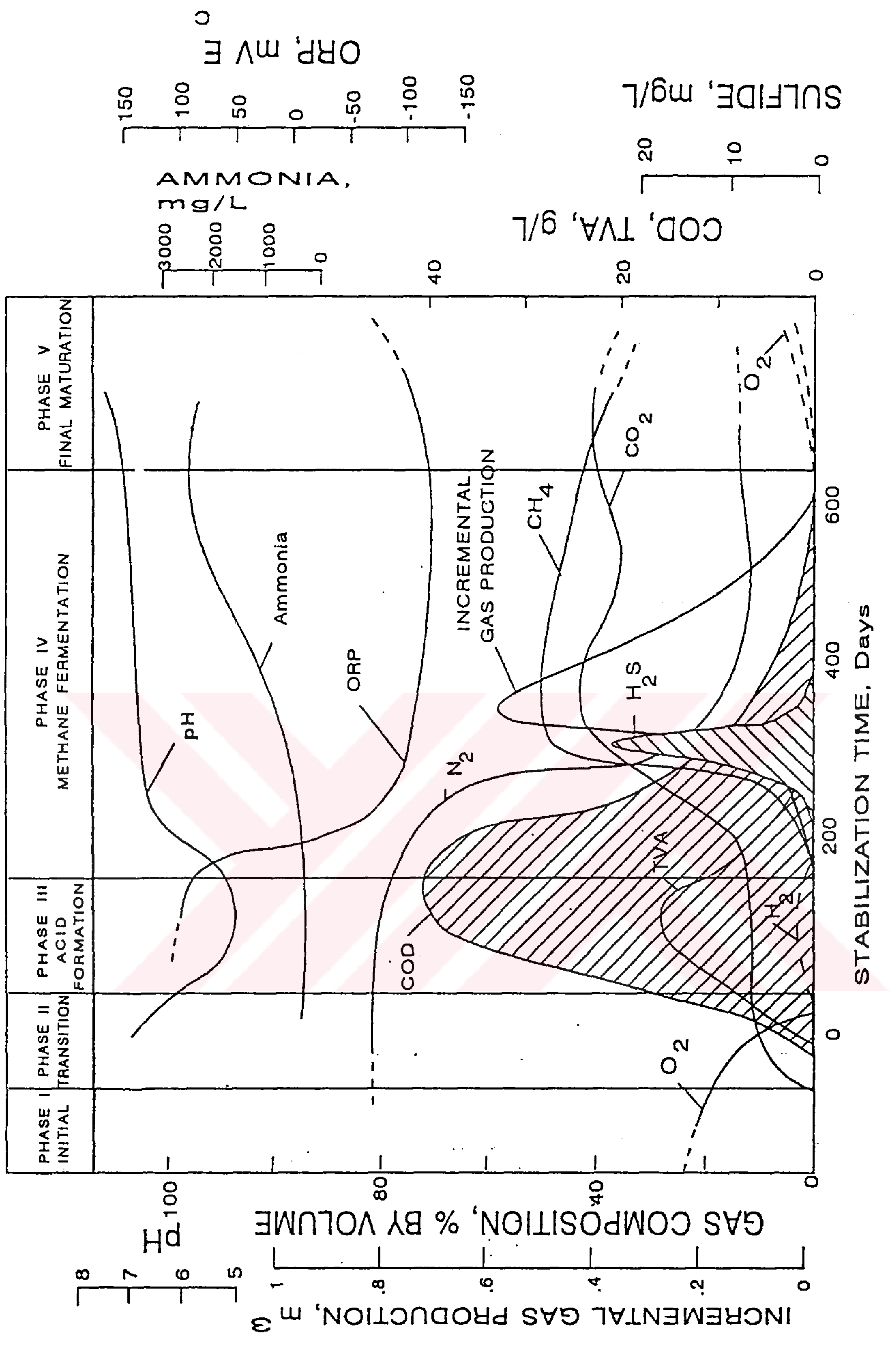


Figure 2.2 Changes in Selected Indicator Parameters During the Phases of Landfill Stabilization (Onay, 1995).

2.1.2 Factors Affecting Landfill Stabilization

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

2.1.2.1 Temperature

Temperature is a key factor for successful anaerobic 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 is 30-37° C (Esteves, 1981). The optimum temperature for thermophilic refuse decomposition reported by Pfeffer is at least 60° C (Barlaz, Ham and Schaefer, 1990). Hartz et al. investigated the impact of the 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 (Hartz *et al*, 1982).

2.1.2.2 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 reported that the optimal pH for methane production is near 7.0 and that reduction in pH occurs in response to an inhibition of methane with a resultant accumulation of organic acids (Farquhar and Rover, 1973). 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 (Arıkan, 1996). Farquhar and Rover reported that an alkalinity in excess of 2000 mg/L as $CaCO_3$ is considered optimum (Farquhar and Rover, 1973).

2.1.2.3 Nutrients

Bacteria in a anaerobic process require a broad spectrum of nutrients for growth and cell maintaince, including carbon, nitrogen, phosphorus, sulfur, 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 is 100:0.44:0.08 and phosphorous is the nutrient most likely limiting the decomposition (Christensen and Kjeldsen, 1989).

2.1.2.4 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). Farquar and Rovers 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(Farquhar and Rover, 1973).Barlaz reported that 55% moisture cannot assure methane production (Barlaz *et al.*,1987).

2.1.2.5 Toxic Substances

The microbial processes in landfills are adversely affected by the presence of toxic substances including high concentrations of ammonia nitrogen, sulfides, 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 the 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 precipitate 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 sulfides, carbonates and hydroxides in the anaerobic processes decreases the toxic effect of heavy metals on methanogens depending on the system pH. Pohland 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 (Pohland, 1992). 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).

2.1.2.6 Input Solid Waste Characteristics

Refuse composition is considered to be important because the nature of the 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. Moreover, particle size of waste influences decomposition rate. Ham and Bookter 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 (Ham and Bookter, 1982).

2.2 SANITARY LANDFILL MANAGEMENT

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. 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. Although conventional landfills consist of cells and lifts with liners, drains, gas vents, leak detection systems and intermediate and final cover, the inadequacy of conventional waste management caused the evaluation of bioreactor landfills which provide rapid, complete attenuation of solid waste constituents and enhance gas recovery. Pohland defined the bioreactor landfill as the modification of conventional landfill with the addition of leachate recirculation and gas management systems (Pohland, 1990). Moreover, Viste described the bioreactor landfill as the "best" alternative which has leachate recirculation within shredded waste (Viste, 1997).

2.2.1 Gas Production and Quality

Landfill gases including mainly CO_2 (carbon dioxide) 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 (Güleç, 1999). 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 environmental 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, 89 ; Pohland, 87).

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).

$$C_aH_bO_cN_d + \left(\frac{4a-b-2c+3d}{4}\right) H_2O \rightarrow \left(\frac{4a+b-2c-3d}{8}\right) CH_4 + \left(\frac{4a-b+2c+3d}{8}\right) CO_2 + d\,NH_3 \quad -2.1$$

The weighted 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 ;

$$1 \text{ g COD}_{\text{organic matter}} = 0.35 \text{ l } CH_4 \text{ at } 0^{\circ}C \text{ and } 1 \text{ bar}$$

By using this assumption ;

$Y_{\text{methane / kg solid waste}} = 0.585 \times 10^6 \text{ g COD} \times 0.35 \text{ l } CH_4 / \text{g COD}_{\text{organic matter}} = 205 \text{ l/ kg MSW}$

MSW = Municipal Solid Waste

From the theoretical 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.

2.2.2 Leachate Production and Management

2.2.2.1 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, 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.

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

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 more 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 the 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 process of landfill stabilization proceed. Leachate can be characterized as a young and old leachate depending upon the phase of landfill stabilization. Acid phase of landfill stabilization is characterized with young leachate, exhibiting a low pH, high organic content as indicated by BOD_5,COD, TOC and total volatile acids (TVA), 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. Characteristic of leachate from old and young landfill are given in Table 2.1

Table 2.1 Typical Data on The Composition of Leachate from New and Mature Landfills (Tchobanoglous et al.,1993).

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

[1] Except pH, which has no unit

2.2.2.2 Leachate Management Strategies

Two principal leachate management strategies exist for landfill operations: the conventional, single pass leaching, "dry" landfill strategy and the newer, leachate recirculation, "wet" landfill strategy (Al-Yousfi and Pohland, 1998).

2.2.2.2.1 Single Pass Leachate Management Strategy

Single pass leachate management entails containment, collection and removal of the 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; full treatment on-site, pretreatment on-site and disposal to a publicly owned treatment works (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 will a very different set of treatment processes than one constructed to treat an old leachate (McBean, Rovers and Farquhar, 1995). That was confirmed by Chian who investigated the stability of organic matter using membrane ultrafiltration, gel permeation 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 finally, a small percentage of organics consisted of high molecular weight humic-carbohydrate-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, organics in stabilized leachate are preferably removed by physical-chemical processes (Chian, 1977).

Physical-chemical treatment methods such as activated carbon adsorption, chemical precipitation, ion exchange and reverse osmosis may become an attractive option for landfill leachate processing, either as a preliminary to biological treatment or as a complete treatment especially for leachate from an older landfill. Keeanan et al. conducted a full-scale physical-chemical treatment of raw sanitary landfill leachate in southeastern

Pennsylvania. 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 better of the heavy metals except copper, for which removal efficiency was 37.9 % (Keenan, Steiner and Fungaroli, 1983).

As concluded by Iza, Keenan and Switzenbaum, 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 (Iza, Keenan and Switzenbaum, 1992).

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. Therefore, treatment costs increase as a function of leachate strength, quantity and available disposal options. Furthermore, due to the insufficiency of moisture content and distribution, stabilization in single pass landfills may require many years to reach the methane phase (Al-Yousfi and Pohland, 1998).

2.2.2.2.2 Leachate Recirculation 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 of enhancing decomposition of organic matters in landfills. Therefore, leachate recirculation may be used ;

- To maximize waste disposal capacity.
- To increase waste biodegradation and gas production and improve waste stabilization.
- To increase leachate management and treatment flexibility.
- To improve leachate quality.
- To reduce leachate treatment cost (Warzinski *et al.*, 2000).

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 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 result in final COD concentrations around 300 mg/L while air stripping of ammonia was very efficient, removing 95% of ammonia (Diamadopoulos, 1994).

Leachate recirculation increases the moisture level of the solid waste and provides accelerated landfill stabilization. Microbial activity is increased at higher moisture content. Churg et al. investigated the effect of recirculated leachate volume on waste degradation. Volume of recirculated leachate was selected to be 2 percent, 10 percent and 30 percent of the initial volume of waste bed in the reactors 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 (Churg *et al.*, 1998). Another similar study was conducted by San 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 (San, 1999).

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

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 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 (Doedens and Cord, 1989).

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. 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 (Townsend et al., 1996).

El-Fadel 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 (El-Fadel, 1999).

2.3 CO-DISPOSAL

2.3.1 The Principles of Co-disposal

Co-disposal is generally defined as the treatment of industrial and commercial liquid and solid wastes by interaction with biodegradable wastes in a controlled landfill (Campbell, 1994). Co-disposal is a technically acceptable method for treating and disposing of certain hazardous wastes with municipal solid waste. However, great attention must be given to the assessment of the types of waste accepted, to the loading rates and to the design of the sites to provide containment for proper management of gaseous and liquid emissions. The principle of developing appropriate loading rates is designed to ensure that;

- The concentration of hazardous substances will not be higher than that observed during disposal of municipal solid waste alone.
- The presence of toxic compounds in the codisposed hazardous waste will not cease biological degradation of municipal waste (Campbell, 1994 ; Cossu and Serra, 1989).

The codisposal of hazardous wastes along with municipal solid waste was studied extensively by Pohland and coworkers (Pohland *et al.*, 1987; Pohland *et al.*, 1993). They used four simulated landfill columns operated with leachate containment, collection and recirculation. Column 1 served as the control column and contained 400 kg of shredded municipal solid waste, while Columns 2, 3 and 4 received 33.6 kg, 65.8 kg and 135.2 kg of alkaline heavy metal plating treatment sludge, respectively, along with 400 kg of shredded municipal solid waste. The experimental results showed that the control column and Column 2 with the lowest sludge loading were very similar and essentially indistinguishable for most parameters, thereby indicating that the 33.6 kg sludge loading did not exceed the microbially mediated assimilative capacity of the system. In contrast, the leachates from Column 3 and 4 showed evidence of severe microbial inhibition, thereby indicating that these higher sludge loadings overtaxed the attenuation mechanism available (Pohland *et al.*, 1987).

Pohland et. al. also conducted another similar study to evaluate the capacity of landfill systems to assimilate and attenuate inorganic and organic priority pollutants codisposed with municipal refuse. Ten simulated landfill columns were operated in pairs. One pair of the columns (one single pass and one recycle) were constructed and loaded with only shredded municipal solid waste. Another one pair were loaded with shredded municipal refuse and organic priority pollutants and three pairs were loaded with shredded municipal refuse, organic priority pollutants and increasing quantities of heavy metals. The results demonstrated that the recycle columns possessed greater assimilative capacity for the organic and inorganic priority pollutants than that afforded by the single pass columns. An explicit inhibition threshold for stabilization consequenced by the priority pollutant loadings was not observed for recycle columns, although retardation was evident for the test column most heavily loaded with heavy metals. In contrast, stabilization in all single pass columns containing organic and inorganic priority pollutant loadings was inhibited (Pohland *et al.*, 1993).

Hazardous wastes can be present in various forms such as liquid, sludge, solid and dusts. Three methods for the application of liquid industrial wastes were developed ; trenching which is normally the preferred method, lagooning and spraying (Watson-Craik and Sinclair, 1995). Barres et.al. conducted a series of laboratory and full scale experiments using different mixing strategies of municipal solid waste and industrial liquid sludge. Five types of industrial sludge including wood screener sludge, formophenolic liquid, metal finishing sludge, oil treatment sludge and urban screener sludge co-disposed with municipal solid waste to study the possibility of the co-disposal of liquid waste and high liquid content waste. The experimental results obtained both in the laboratory tests and in the field studies indicated that co-disposed industrial liquid sludges did not cause any significant change in the chemical composition of landfill effluents and induced only a slight and transitory further pollutant flow to that already generated by the municipal solid waste alone (Barres *et al.*, 1988).

Co-disposal relies upon an active biological mass to degrade and render inert hazardous elements of waste input. The nature of the wastes must be such that methanogenesis can be established within the site before co-disposal commences because under methanogenic conditions involving near neutral pH conditions, both the degradation of organic compounds present in co-disposed wastes such as phenols and the precipitation of metals as insoluble compounds limit the movement of waste contaminants into leachates (Greedy, 1993; Campbel, 1994).

2.3.2 The Co-disposal of Heavy Metals

A metal is an element that will give up one or more electrons to form a cation in an aqueous solution. The term heavy metal is used to denote the metals which are toxic. Heavy metals reach the sanitary landfill by co-disposal of industrial wastes, incineration ashes, mine wastes and disposal of 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, cadmium, copper, zinc and nickel.

Iron exists in the ferric (Fe^{+3}) or ferrous (Fe^{+2}) form, depending upon the pH and dissolved oxygen concentration (Eckenfelder, 1989). Under strongly reducing conditions in landfills, iron exist in ferrous state. In the +2 oxidation state, iron is characterized by its fairly high solubility at pH levels below 9 and the potential for forming sparingly soluble sulfides (FeS, pK_{so}= 18.6) (Pohland *et al.*, 1993).

Cadmium, Nickel and Zinc can be treated together due to their considerable degree of similarity. 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 the 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.

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). 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).

The solubility of metals in the leachate of landfills depends on the parameters pH, redox potential, solubility of the deposited metal species, concentration of complexing agents (NH_3/NH_4^+, humic acids) and ion strength (Förstner *et al.*, 1991). Metal solubilities in leachate increase as pH decreases, thus, the highest metal concentrations should be observed during the Acid Formation Phase when pH values are at a minimum. This was reflected with Table 2.2 which depicts the heavy metal concentrations in acidogenic and methanogenic phases.

Table 2.2 Concentrations of Heavy Metals (μg/L) in Leachates from Sanitary Landfills (Förstner *et al.*, 1991).

Element	Acetic Phase		Average	Range	Methanogenic Phase	
	Average	Range			Average	Range
Iron	780	20-2100			15	3-280
Manganese	25	0.3-65			0.7	0.03-45
Zinc	5	0.1-120			0.6	0.03-4
Arsenic			160	5-1600		
Cadmium			6	0.5-140		
Chromium			300	30-1600		
Copper			80	4-1600		
Lead			90	8-1020		
Mercury			10	0.2-50		
Nickel			200	20-2050		

2.3.3 The Attenuation Mechanisms of Co-disposed Heavy Metals

Co-disposal aims to reduce the potential negative impact of hazardous waste both by simply diluting it with municipal waste and by taking advantage of attenuation mechanisms present inside landfill (Cossu and Serra, 1989). These attenuation mechanisms for heavy metals are adsorption, acid-base, oxidation-reduction, precipitation/complexation reactions (Pohland *et al.*, 1988).

2.3.3.1 Adsorption

The removal of heavy metals from landfills are dependent on several different processes occurring inside the landfills. One important process is the adsorption of heavy metals onto the waste. However, there are no 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 (Watson-Craik and Sinclair, 1995).

2.3.3.2 Acid-Base

The pH is 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 acid formation and consumption will significantly influence pH and associated heavy metal solubility.

2.3.3.3 Oxidation-Reduction

Oxidizing materials are often considered hazardous as they are toxic and may cause ignition or explosition (Greedy, 1995). However, 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 (VII)/ MnO_2/ Mn^{-2}, Fe^{-3}/Fe^{-2}, Cr (VI)/ 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 (Byoung-Young, 1989). Figure 2.3 is a pH-Ec diagram for the sulfate- sulfide system and indicates conditions necessary to favor the presence of sulfide.

2.3.3.4 Precipitation / Complexation

Under anaerobic conditions soluble metals precipitate as insoluble sulfides, carbonates, hydroxides, and, possibly, phosphates in the landfills (Pohland, 1991). 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).

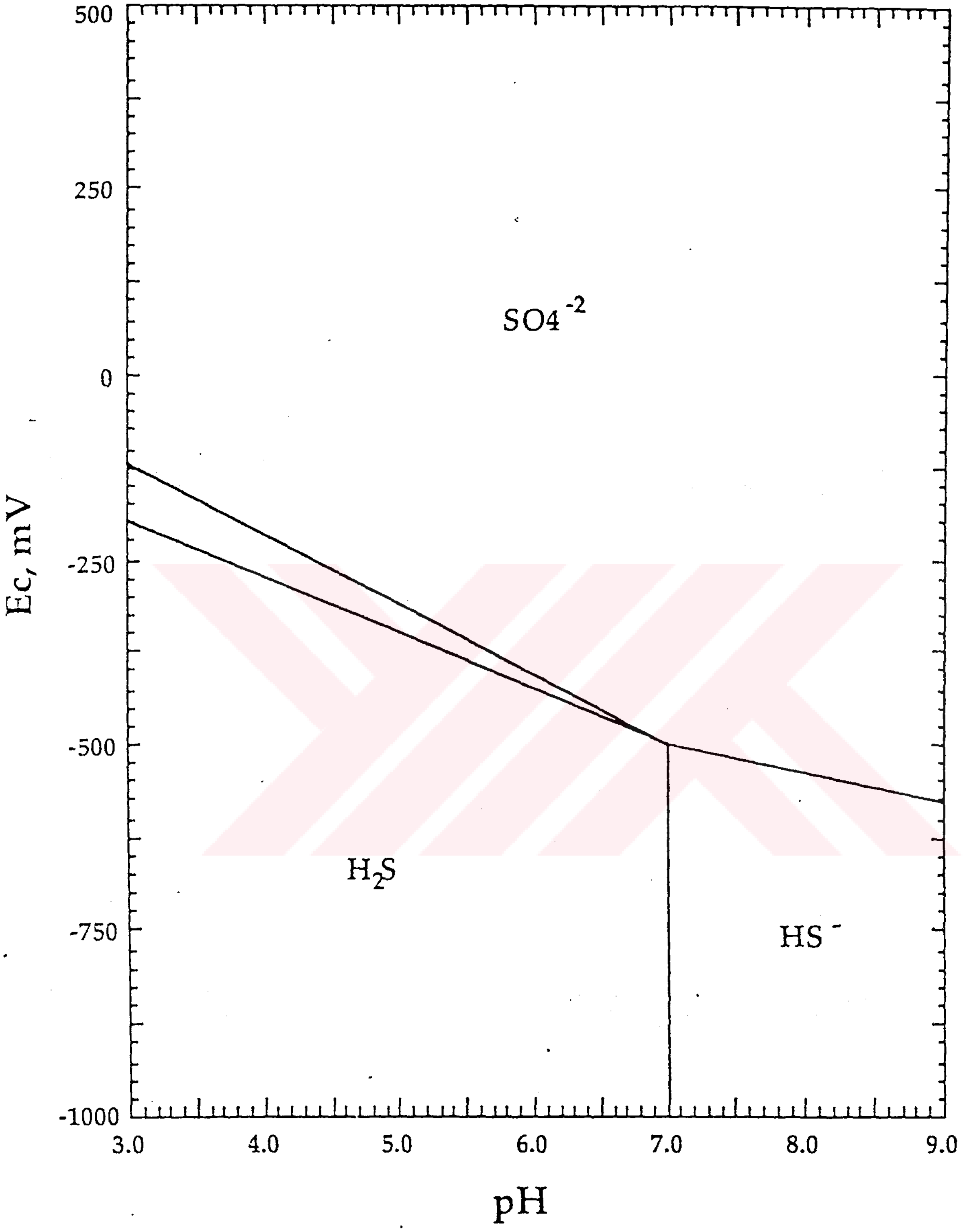


Figure 2.3 Ec-pH Diagram For The $SO_4^{-2}/S^0/S^{-2}$

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. Therefore, during methane fermentation, with more elevated ORP and near neutral pH, leachate chromium concentrations are excepted to decrease below detectable levels (Pohland, 1991).

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).

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 in 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 and 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 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 (Jalali and Baldwin, 2000).

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.

$$H_2S \leftrightarrow H^- + HS^- \leftrightarrow 2\ H^- + S^{-2} \qquad (2.2)$$

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 (Hilton and Oleskiewicz, 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).

$$Me^{+2} + S^{-2} \rightarrow MeS \qquad (2.3)$$

where Me is taken as the symbol for a metal

Figure 2.3 represents solubility of several metals in equilibrium with a 0.02 M total concentration (Ct) of sulfides, where Ct is defined as ;

$$Ct = (H_2S) + (HS^-) + (S^{-2}) \qquad (2.4)$$

From this Figure, it is obvious that the saturation solubilities of these metals are very low in spite of being in equilibrium with correspondingly low concentrations of S^{-2} (Pohland *et al.*, 1987).

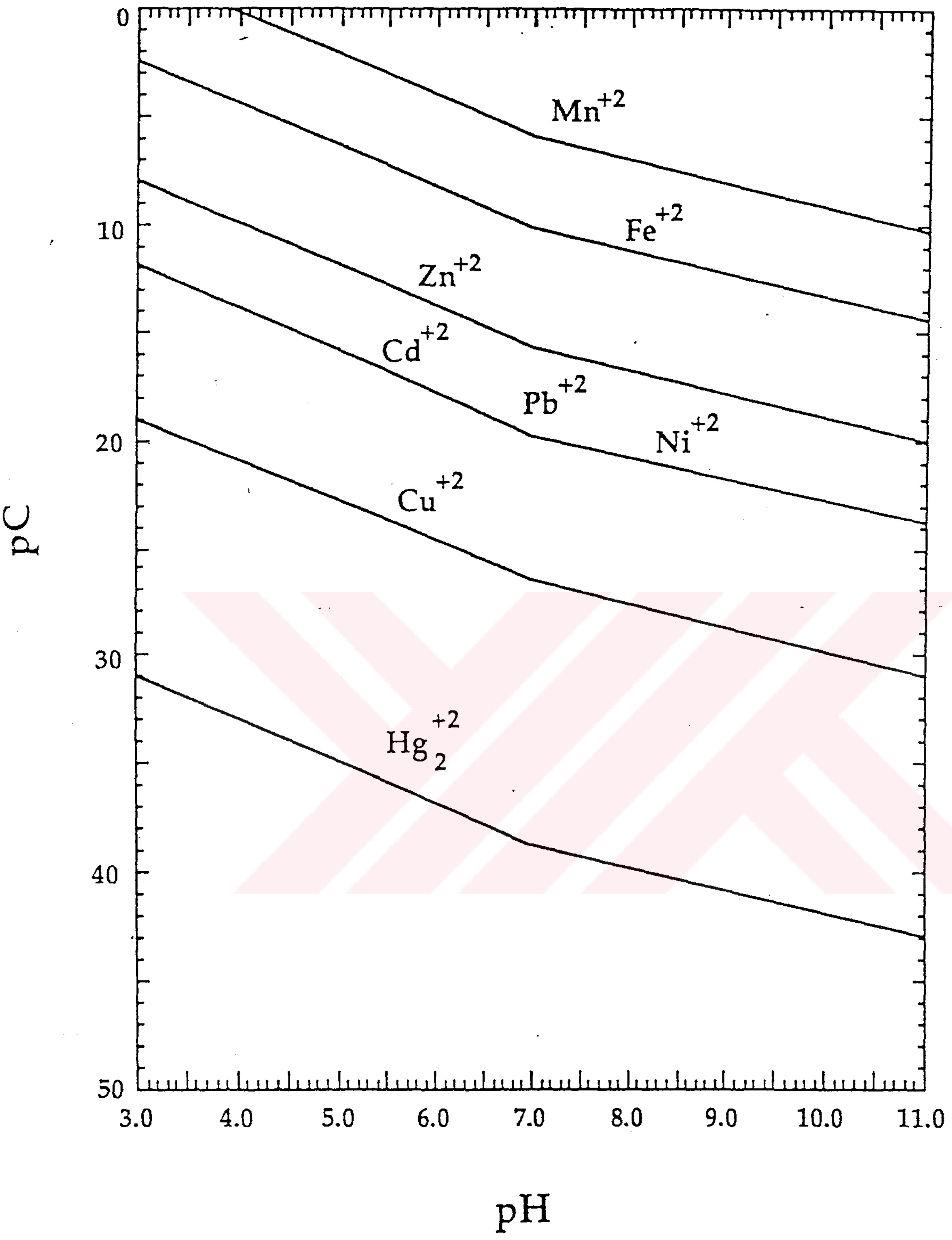


Figure 2.4 Solubility of Several Heavy Metals Under Sulfide Control (Sulfide C= 0.02 M)

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).

3. MATERIALS AND METHODS

3.1 Configuration of the Simulated Landfill Reactors

Two 96-liter PVC reactors for single pass leaching and leachate recycle operations were used in the laboratory. Each reactor had a diameter of 0.35 m and a length of 1 m. The design and operational features of the single pass and recycle simulated landfill bioreactors are presented in Figure 3.1

The reactors were equipped with three ports; one port was used for drainage and sampling while the 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. In case of the recycle reactor, 0.75 cm Masterflex ® hose attached to other end of the tee was connected to the leachate plastic container and functioned as a leachate recycle line. In case of the single pass reactor other end of the tee was capped with rubber septum and sealed with silicon. A PVC tee was placed in the 1 cm diameter hole. One end of the tee was attaché by 0.75 cm Masterflex ® hose. The hose was connected to the leachate plastic 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. All connections to the reactors were sealed with silicone sealant and epoxy glue.

A leachate distribution system made of PVC sheet was used at the center of the top lid to provide uniform leachate distribution onto the waste matrix as indicated in Figure 3.2. Three square PVC sheets with dimensions of 7.5 cm long, 7.5 cm wide, and 0.8 cm thick

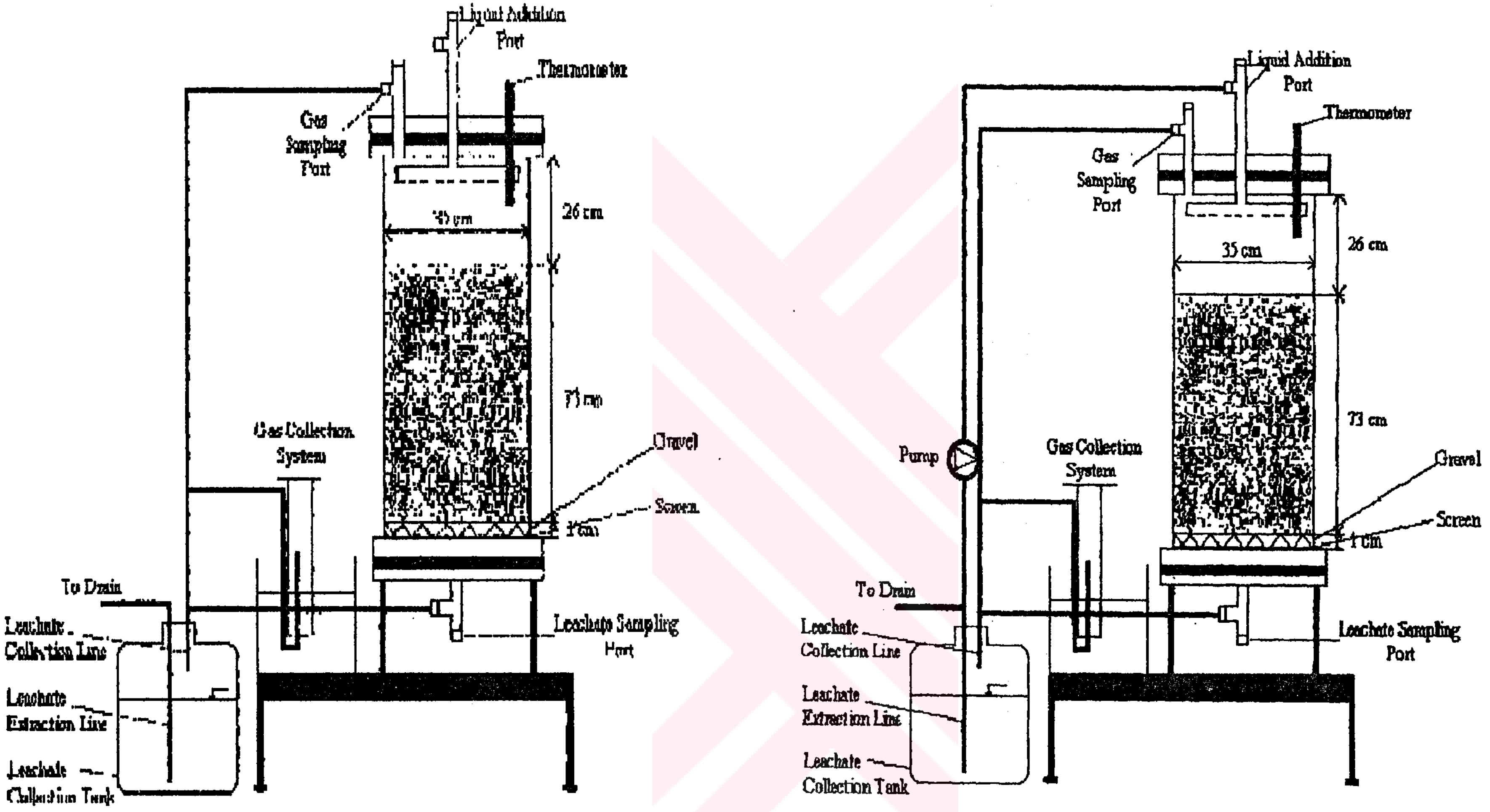
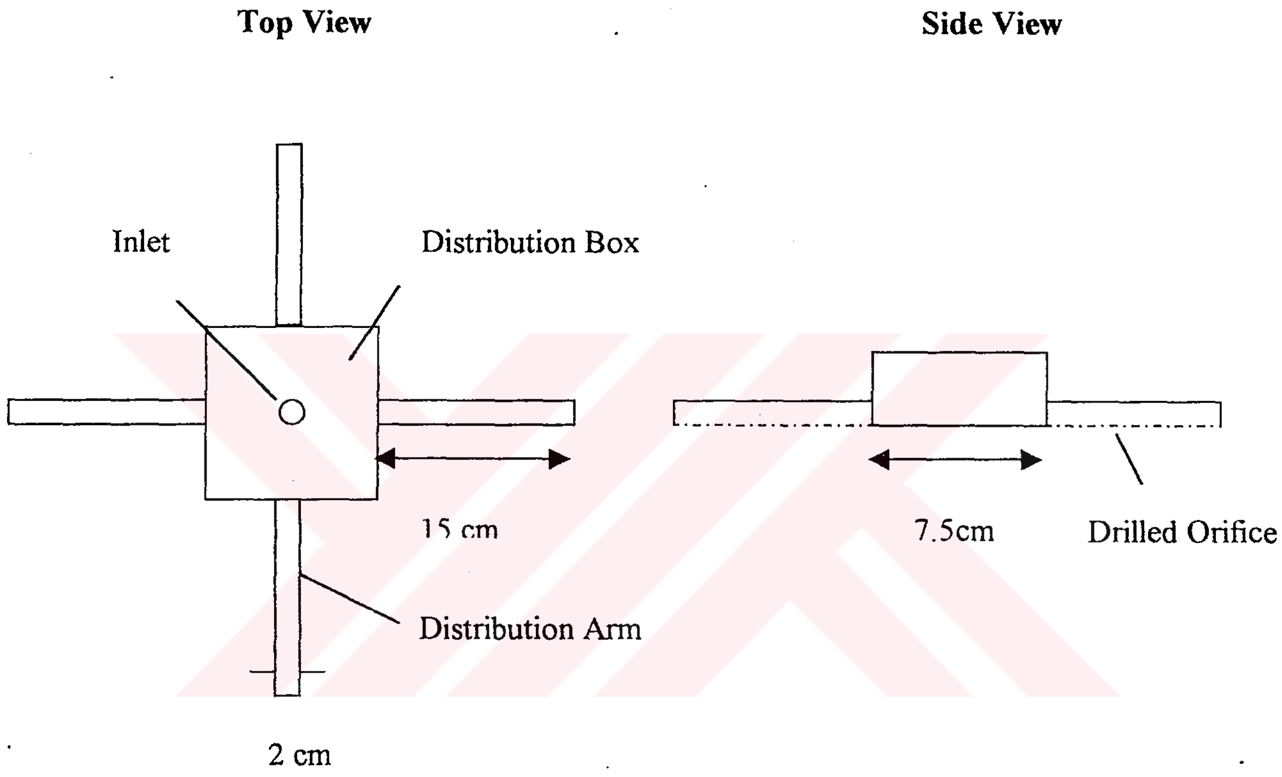


Figure 3.1 The design and Operational Features of the Single Pass and Recycle Reactor

were glued together to form the distribution box with 2 cm holes on five faced. Four 2-cm diameter PVC pipes with 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.



(NOT TO SCALE)

Figure 3.2 Leachate Distribution System

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

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

The gas produced from reactors was measured by using liquid displacement technique. A 2-L cylinder was placed in the vessel in an inverted position and filled with confining solution (20% $NaSO_4$ and 5% H_2SO_4 by weight) to minimize the dissolution of CO_2 and CH_4 in the liquid. The volume of daily displaced liquid in the cylinders was recorded as the daily gas production.

3.2 The Characteristic of Waste Matrix in the Simulated Landfill Reactors

The reactors that were constructed, loaded and initiated to operate in previous leachate recycle research were maintained to study for the objective of this research. Each reactor was loaded with shredded and compacted solid waste mixture of approximately 13 kg and 1 liter of anaerobic digested sludge obtained from Tekel Rakı factory in Beykoz-Istanbul to initiate and enhance solid waste stabilization.

Shredded solid waste in the reactors were prepared synthetically to assure accelerated stabilization, establish the identity and maximize the homogeneity of the refuse. The synthetic solid waste mixture represents typical solid waste composition determined for Istanbul region as indicated in Table 3.1. Moreover, Table 3.2 presents the existing characteristic of shredded solid waste and anaerobic sludge in the simulated landfill reactors prior to the commencement of the experimental study.

Table 3.1 Synthetic Solid Waste Composition (San, 1999)

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

Table 3.2 The Existing Characteristic of Shredded Solid Waste and Anaerobic Sludge in the Simulated Reactors (San,1999).

PARAMETER	SOLID WASTE IN THE REACTORS		ANAEROBIC SLUDGE
	SINGLE PASS	RECYCLED	
Moisture Content %	78	75	-
Density kg/m^3	178	178	-
Solid %	-	-	1.69
Volatile Solids % dry	-	-	88

3.3 Simulated Landfill Operation

The purpose of this study was to develop an understanding of heavy metal attenuation in codisposal landfill simulating reactors by means of precipitation by sulfide compounds. For this purpose, the experimental period was divided into two operational phases.

In the first phase of operation, it was aimed to establish methanogenic conditions in both reactors before the codisposal of heavy metals. Since low pH values in landfills in acidogenic phase cause solubilization and mobilization of heavy metals, methanogenesis must be established within the landfill site to form insoluble metal complexes under the reducing environment at neutral pH values. With this approach, the first phase started on February 2, 2000 after switching the two leachate management strategies, leachate recirculation and single pass leaching, between reactors. Reactors were sealed with silicone to prevent gas leakage. The purpose of this exchange was to accelarate and establish the activity of methanogenic population in the reactor in the acidogenic phase and to provide the identical environmental conditions in both reactors because the reactor operated as single pass was kept in acidogenic phase while the other operated as recycle reactor was forced into methanogenic phase in previous research. Throughout Phase 1, separately sub-operational stages was applied to the reactors which are explained in the following section and summarized in Table 3.3 to facilate the desired methanogenic conditions in the reactors.

Table 3.3 Operational Stages Employed Throughout the Experimental Study

STAGE	THE RECYCLE REACTOR						THE SINGLE PASS REACTOR			
	DAYS	RECIRCULATED LEACHATE VOLUME (mL)	FREQUENCY	WATER ADDITION (mL)	FREQUENCY	ADDITIONS	DAYS	WATER ADDITON (mL)	FREQUENCY	ADDITIONS
1	0-103	1000	1/week	500	1/week	between Day 56 and 84, KOH	0-114	500	1/week	
2	103-138	1000	2/week	500	1/week	recycle from SP to RR[1]	114-205	500	1/week	adding increasing organic load
3	138-170	1000	3/week	500	1/week	between Day 142 and 156, 100 g/L Na_2CO_3	205-245			no simulated rainfall addition
4	170-307	1000	1/week	500	1/week	on Day 245, 1L metal solution	245-307	500	1/week	on Day 245, 1L metal solution

[1] SP: single pass reactor RR: recycle reactor

Table 3.4 The Existing Leachate Characteristics Used for Operational Stages

PARAMETERS (1)	THE RECYCLE REACTOR					THE SİNGLE PASS REACTOR	
	Stage 1		Stage 2	Stage 3	Stage 4	Stage 1	Stage 4
	RR (2)	RR Container (3)	SP Container (4)	RR Container (5)	Before Codisposal RR (6)	SP Reactor (7)	Before Codisposal SP Reactor (8)
pH	5,61	5,79	7,76	6,91	6,99	7,78	7,14
Conductivity (mS/cm)	—	—	—	—	3,37	—	4,14
ORP (mV)	-137	-135	-234	-284	-91	-174	-152
COD (mg/L)	10020	26536	721	11109	1309	1159	290
BOD_5 (mg/L)	—	—	—	—	98	—	17
BOD_5/COD	—	—	—	—	0.075	—	0.059
Alkalinity (mg/L)	2493	2592	4829	2700	1631	4038	2531
SO_4^{-2} (mg/L)	0	75	0	0	0	0	0
Sulfide (mg/L)	40	35	21	—	3,40	12	3,6
Chloride (mg/L)	410	482	446	315	87	371	68
NH_3-N[1] (mg/L)	—	574	233	—	—	—	—
PO_4-P (mg/L)	171	285	30	81	22	56	37
Leachate volume (L)	—	14	16,5	5	—	—	—

[1] on Day 113 of operation, NH_3-N concentrations in recyled reactor and single pass reactor were 302 and 241 mg/L, respectively.

SP:single pass RR: recyle reactor

After ensuring the onset of the methanogenic conditions in both reactors as indicated in columns 6 and 8 of Table 3.4, the second phase operation was begun by the addition of the selected heavy metals into the simulated landfill reactors on Day 245. The five heavy metals including iron, copper, nickel, cadmium, zinc were considered to be the most common heavy metals disposed into landfills. Therefore, knowledge of their behavior and mobility in landfills and the effect of sulfide compounds on these metals were the major concerns of this study. Based on this criteria, the selected metals (Fe, Cu, Ni, Cd, Zn) were prepared by dissolving the metal salts in one liter deionized water and introduced into the reactors according to the quantities suggested for co-disposal under the directives of the Turkish Hazardous Waste Control Regulation to prevent inhibition of the microbially mediated processes during waste stabilization. The regulation is presented in Table C-1 of Appendix C and also summarized in Table 3.5. When the metal solution was prepared in stoichiometric amounts, the sulfate salts of these metals except zinc were used in order to better understand precipitation mechanisms of metals together with sulfide compounds in landfills. Moreover, the metal sulfates were loaded in a manner which does not exceed the toxic sulfide level of 200 mg/L (Pohland, 1992) after reduction of sulfate to sulfide and precipitation of sulfide by heavy metals. Table 3.5 presents this calculated theoretical masses.

Table 3.5 The Masses of the Selected Heavy Metals Loadings into the Reactors[1]

The Selected Heavy Metals and Their Salts	Required Masses for Selected Metals (gr)	The Amount of Metal Salts (gr)	Loaded Sulfide with Metal Salts (gr)	The Amounts in the Regulation (gr/ton MSW)[2]
Cu / $CuSO_4.5H_2O$	1.3	5.1070	0.6560	100
Ni / $NiSO_4.6H_2O$	1.3	5.8205	0.7087	100[3]
Cd / $CdSO_4.2.5H_2O$	0.13	0.2930	0.0370	10
Fe/$(NH)_4Fe(SO_4)_2.6H_2O$	2.0	14.0040	2.2856	200
Fe / $FeCl_3.6H_2O$	0.6	2.8960	-	
Zn / $ZnCl_2$	1.3	2.7089	-	100

[1] gr metal/ kg wet shredded municipal solid waste

[2] MSW : municipal solid waste

[3] the Regulation does not suggest a special amount for Nickel but it suggests 100 gr/ton for all heavy metals as a general approach

3.3.1 Operation of the Recycle Reactor

As indicated in Column 2 of Table 3.4, the initial condition of recycle reactor was acidogenic. Therefore, the recycle reactor was operated to enhance the activity of the methanogenic population and to provide the same environmental conditions with the single pass reactor under four operational stages. These operational stages are presented in Table A-1 of Appendix A and are summarized in Table 3.3.

The first operational stage wast started by the weekly recirculation of 1 L leachate and weekly water addition of 500 mL water, (corresponding to an equivalent of 20 cm/year rainfall). For the acceleration of waste stabilization and prevention of possible acid inhibition on the methanogens, a buffer solution of 1N KOH was employed as weekly from Day 56 to 84 within the first stage. However, towards the end of the operation stage, the addition of 1N KOH was stopped because potassium cation reached to a moderately inhibitory level of 3000 mg/L in the reactor. A total of 970 mL 1N KOH was introduced into the reactor during this stage.

In the second stage of operation, recirculation frequency in the recycle reactor was increased from one to two times per week, one time from single pass reactor within the methanogenic conditions and one time from the inside of its own. The characteristics of single pass container are given in column 4 of Table 3.4. The aim of this external recyle of one liter-leachate was to establish desirable microbial population in the recycle reactor and initiate accelerated waste stabilization.

After the introduction of methanogenic population into the recycle reactor, the recirculation frequency was increased to three times per week and a buffer solution of sodium carbonate (Na_2CO_3) was added throughout the third stage in order to enhance the growth of methanogens. The objective of sodium cation selection as buffer solution was to reduce the toxicity of potassium cation because of the antagonistic effects of sodium and potassium cations. The buffer addition was practiced by the neutralization of recirculated leachate to pH 7-7.5 using a 100 g/L Na_2CO_3 solution. A total of seven additions of Na_2CO_3 were made from Day 142 to Day 156 and at the end of the buffer addition, potassium and sodium cations were 2086 and 227 mg/L, respectively. Column 5 of Table

3.4 reflects leachate characteristics of the container of the recycled reactor which provided leachate into the reactor throughout this recirculation operation.

In the last stage, the recirculation frequency was readjusted to one time because the desired anaerobic conditions in the recycle reactor were established. The fourth stage of operation lasted until the end of the experiments. Throughout the all stages, distilled water was applied to the reactor at a constant rate of 500 mL/week for the simulation of precipitation.

3.3.2 Operation of the Single Pass Reactor

As indicated in Column 7 of Table 3.4, the initial condition of single pass reactor was methanogenic. Like the recycle reactor, the single pass reactor was also operated under four operational stages to keep methanogenic phase. These operational stages are given in Table A-1 of Appendix A and summarized in Table 3.3

The first stage was conducted until Day 114 along with the addition of 500 mL of water for the simulating of rainfall in order to provide conventional single pass leaching management. Since the required organic carbon sources for methanogens were washed out quickly from the system, additional organic carbon was provided from the other reactor during the second stage of operation. The organic carbon was introduced to the reactor in two way: within simulated rainfall , with direct recycle from the recycle reactor. During the third stage operation, water addition was stopped from Day 205 to Day 245 in order to prevent washout in systems. Along with the beginning of Phase2, the fourth stage of operation was conducted by only simulated rainfall addition until the end of the experiments.

3.4 Sampling and Analytical Methods

The collected leachate and gas samples were monitored on a regular basis to understand the degree of waste stabilization in the bioreactors and the fate of the selected heavy metals. Leachate samples collected from the bottom of the single pass and recycle bioreactors were analyzed for chemical oxygen demand (COD), pH, oxidation-reduction potential (ORP), conductivity, alkalinity, sulfate, sulfide, phosphate, chloride and selected heavy metals (Fe, Cu, Ni, Cd, Zn). 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-WPCF, 1992).

COD is a key parameter to determine the organic strength of leachate. COD analysis was made by the dichromate closed reflux method. 2.5 mL diluted leachate samples were pipetted in to HACH vials containing 1.5 mL of potassium dichromate and 3.5 mL of acid digestion mixture. The vials were placed into HACH COD digester and digested for two hours at 150°C. After this step, the digested samples were measured by HACH Portable Water Analysis Instrumentation DR/3 Spectrophotometer.

The pH values of the reactors were monitored routinely during the experimental period due to its importance as indicative parameter in waste stabilization. pH of samples was measured by a pH probe attached to a ORION SA 520 pH meter after calibration with pH 4, pH 7 and pH 10.

ORP is physical-chemical parameter that indicates the oxidation-reduction potential of the system. A ORP probe attached to a ORION SA 520 pH meter was used for determination of the ORP.

Conductivity is a measure of the ability of an aqueous solution to carry an electric current. Conductivity of samples was measured by a probe attached to a WTW LF 320 conductivity meter.

Alkalinity was monitored according to the Titration method (2320 B), outlined in the Standard Methods for the Examination of Water and Wastewater 1992.

Sulfate was monitored using Sulfaver 4 HACH method. Pillows containing Sulfaver 4 powder were poured into 25 mL of sample and allowed 5 minutes to develop turbidity. Sulfate concentration is known to be proportional to the developed turbidity, as determined using HACH Portable Water Analysis Instrumentation DR/3 Spectrophotometer. Sulfide was measured using Titrimetric (Iodine) method where the sample was titrated by sodium thiosulfate . The end point of titration was detected by starch solution.

Orthophosphate present in the leachate were determined by the Ascorbic Acid Method. Pillows containing phosphate reagent were poured into 25 mL of sample and the absorbance of the sample was measured at 880 nm using HACH Portable Water Analysis Instrumentation DR/3 Spectrophotometer after color development.

Chloride was measured by Argentrometric Method where the sample was titrated by silver nitrate ($AgNO_3$). The end point of titration was detected by potassium chromate indicator.

The selected metals (Fe, Cd, Cu, Ni, Zn) were also monitored using a Perkin Elmer Atomic Absorption Spectrophotometer. Prior to analysis, each sample was digested with concentrated HNO_3 and (1:1) HCl according to the standard method ASTM (3010). During this research, total metal concentrations were measured.

The gas produced in the reactors was collected and analyzed for quantity and composition. The volume of gas produced was determined daily by observing the displacement of the confining solution in gas collection units. The gas composition analyses were performed at Yıldız Technical University Department of Chemical Engineering. The analysis started at 24.03.2000 on the Day 51. The samples were carried with 2.5 mL insulin syringe. The general gas composition was analyzed once a week. The percentage of methane and carbon dioxide in the biogas was determined by using a gas chromatograph (GC), Shimadzu –9A equipped with a thermal conductivity detector (TCD) and a 2-m mesh Propac Q column. The operational temperature of injection port, the oven and detector were 50, 80, 80 °C, respectively. Helium was used as the carrier gas at a flow rate of 2mL/min. Calibration was made using 99.99 % Supelca methane standard and 5 % gas mixture.

The methods used for the gas and leachate analysis from simulated landfill reactors are summarized in Table 3.6.

Table 3.6 Methods Used for Leachate and Gas Analyses from the Simulated Landfill Reactors

PARAMETER	METHOD	INSTRUMENT	REFERENCE
pH	4500-H B Method Electrometric	ORION SA 520 pH meter	APHA, AWWA-WPCF (1992)
ORP	2580 B Method	ORION SA 520 pH meter	APHA, AWWA-WPCF (1992)
Conductivity	2510 B Method	WTW LF 320 conductivity meter.	APHA, AWWA-WPCF (1992)
COD	5220 D Method Closed Reflux, Colorimetric	HACH COD digester ; HACH DR/3 Spectrophotometer.	APHA, AWWA-WPCF (1992)
Alkalinity	2320 B Method Titration		APHA, AWWA-WPCF (1992)
Orthophosphate	4500-P E Method Ascorbic Acid	HACH DR/3 Spectrophotometer	APHA, AWWA-WPCF (1992)
Chloride	4500-Cl B Method Argentometric		APHA, AWWA-WPCF (1992)
Sulfate	4500-SO_4^{-2} E Method Turbidimetric	HACH DR/3 Spectrophotometer	APHA, AWWA-WPCF (1992)
Sulfide	4500-S^{-2} E Method Iodometric		APHA, AWWA-WPCF (1992)
Heavy Metals	ASTM 3010	Perkin Elmer Atomic Absorption Spectrophotometer.	
Gas Production	Water Displacement		
CH_4, CO_2	Gas Chromatograph	Gas Chromatograph (GC), Shimadzu –9A	

4. RESULTS AND DISCUSSION

4.1 GAS ANALYSIS

Gas volume and composition are main indicators of the progression of landfill stabilization process. Methane and carbon dioxide are the major products of anaerobic solid waste decomposition . The results of gas production as daily and cumulative and gas composition are given in Figures 4.1 through 4.6 and presented in Tables of Appendix B.

4.1.1 Gas Production

Daily gas volumes produced in the recycle and single pass reactors are given Figures 4.1 and 4.2, respectively. Cumulative gas volumes produced in the recycle and single pass reactors are given in the Figures 4.3 and 4.4, respectively.

Daily gas production was determined by measuring the volume of daily displaced liquid in the cylinders. Therefore, the capacities of gas collection units played an important role in the readings of daily gas productions. When the capacity of the gas collection unit was exceeded, daily gas production was measured as equal to the maximum capacity of cylinders. As a consequence, the actual gas production could not be determined especially during the first stage of single pass reactor and the fourth stage of recycle reactor. The actual gas productions were higher than the recorded values.

During the first phase, the initial gas production rates of the recycle and single pass reactors were 500 and 2000 mL, respectively. The reason of the higher gas production amount in the single pass reactor was due to the preestablished methanogens developed in the previous research. On the other hand, the gas production in the recycle reactor was lower due to the prevailing acidogenic conditions and a slight decrease was observed when acid conditions became more intense after the recirculation of leachate having high organic content. Along with the addition of 1 N KOH to buffer the leachate pH, the gas production rate in the recycle reactor increased from 200 mL to 1000 mL. However, gas production ceased in both reactors between Day 79 and Day 92 due to the decrease in the room temperature to 19°C related to the technical problems with the heater. After the maintenance of the heater, ceased gas production was begun to increase on Day 93. This unwanted condition showed the important effect of temperature on the activity of microorganisms. Moreover, stopping the addition of 1N KOH on Day 84 resulted in decrease in gas production until the exchange of leachate between the reactors. During the second stage, the daily gas production of the recycle reactor was in the range of 800-1000 mL range and the same gas production trend continued until the middle of the third stage. After the enhancement of microorganisms by the addition of Na_2CO_3, a sharp increase on Day 156 was observed. Along with the initiation of methanogenic conditions, the gas production rate reached to its highest value of approximately 5000 mL through the fourth stage.

In contrast to the recycle reactor, in the single pass reactor, a decrease in gas production through the experiments was observed due to nearly completed stabilization of the readily degradable organic carbon sources. The gas production was not measured in the single pass reactor between Day 79 and Day 92 as a result of the decrease in the temperature. During the second stage, as indicated in Figure 4.2, an attempt was made to prevent substrate deficiency in the reactor. However, an increase in gas production was not observed except several fluctuations but it prevented a rapid decline of the organic substances. After the second stage, the gas production stayed approximately constant and was measured less than 100 mL until the end of experiments.

During the second stage, after the addition of dissolved metal salts into the reactors, the gas production rate did not change in both reactor. Therefore, initial high heavy metal concentration did not possess toxic effects on microorganisms.

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. The total gas produced in the recycle reactor was much more greater than that in the single pass reactor. While the recycle reactor produced about 354 L, the single pass reactor produced 183 L of gas. In the recycle reactor, recirculation of leachate intensified the microbial activity by reintroducing

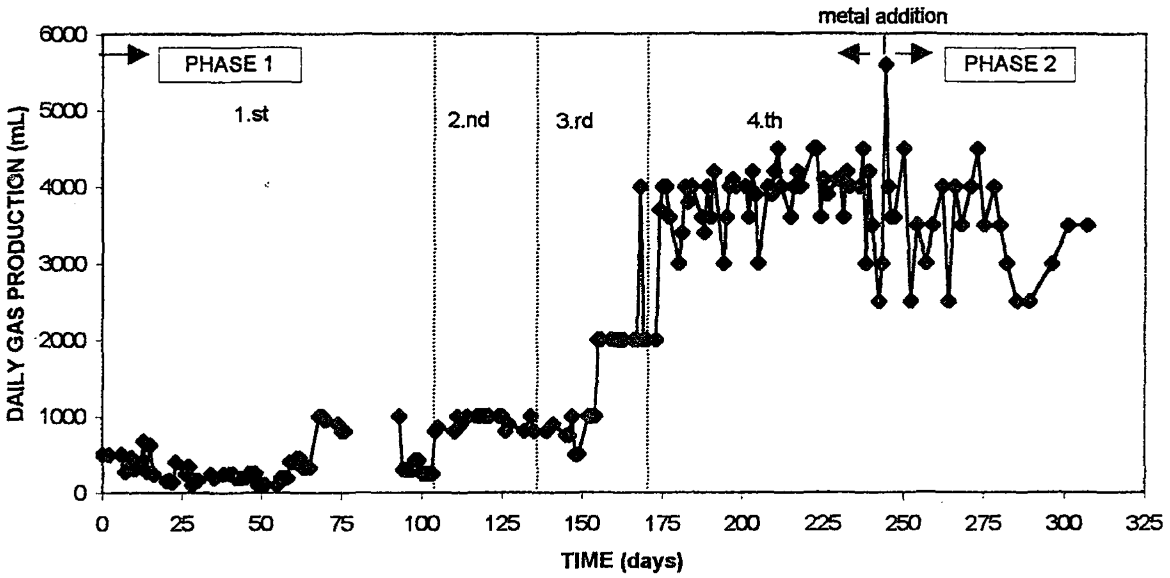


Figure 4.1 Daily Gas Production from the Recyle Reactor

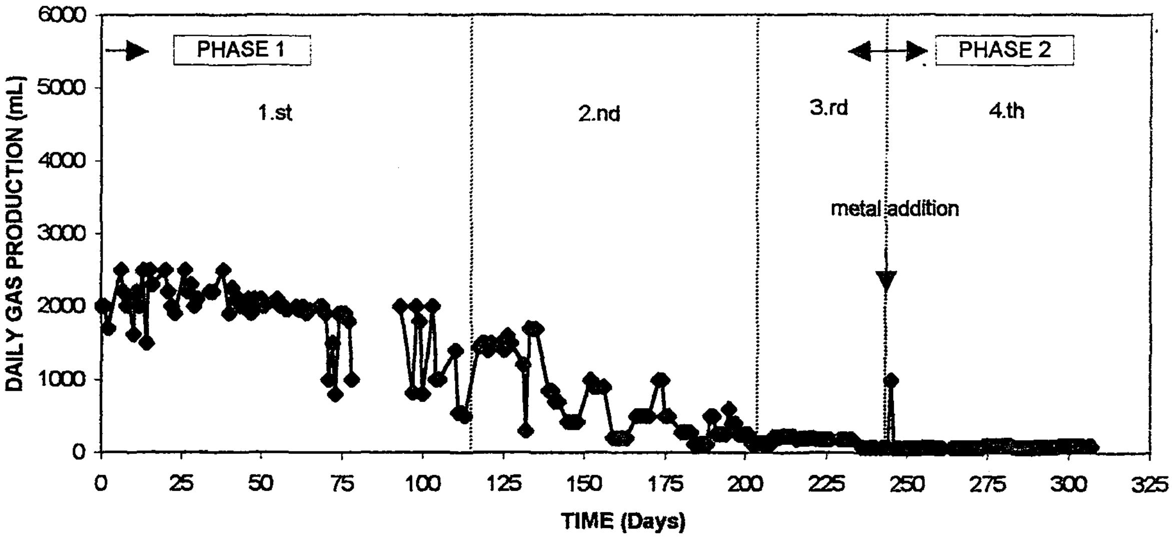


Figure 4.2 Daily Gas Production from Single Pass Reactor

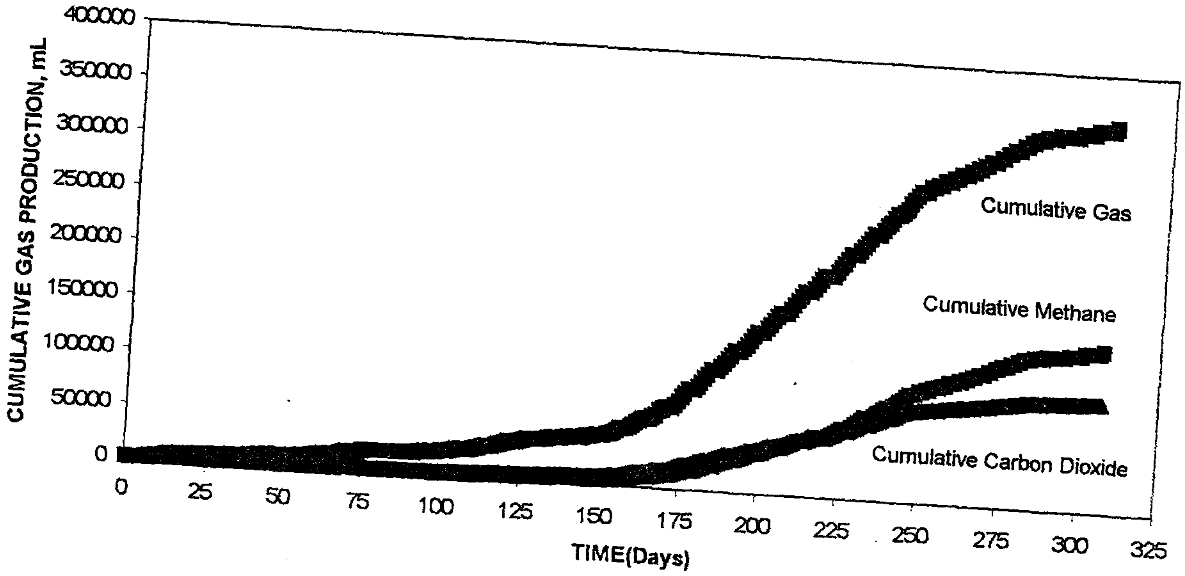


Figure 4.3 Cumulative Gas Production from the Recycle Reactor

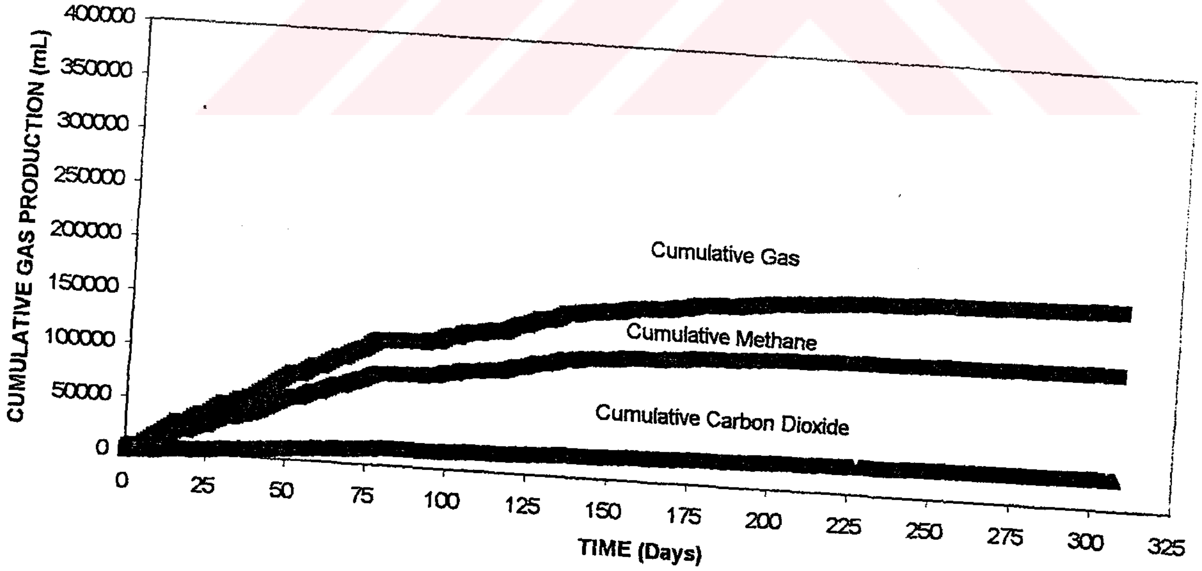


Figure 4.4 Cumulative Gas Prodution from the Single Pass Reactor

the nutrients, homogenizing the environment and allowing better contact bacteria and substrate. As a result, conversion of acids and stabilization of waste was enhanced, as indicated by the increase in the gas volume produced. On the other hand, in the single pass reactor, a decrease in the gas production was observed because the stabilization of the readily degradable organic sources was completed nearly and necessary substrates were washout from the reactor.

4.1.2 Gas Composition

Methane and carbon dioxide are the principal gases produced during the decomposition of organic fraction of waste. Change in the concentration of methane and carbon dioxide reflects the rate of biological activity and organic material conversion. The gas composition for the recycle and the single pass reactor are given in Figures 4.5 and 4.6, respectively.

Gas samples were measured at Yıldız Technical University due to the absence of Gas Chromatography in the Institute of Environmental Sciences Laboratory. As a consequence of poor sampling and storage technique it was difficult to obtain the samples without introducing the air. Although results are not accurate and can not be used to determine the quantity of gas constituents, they can be used for qualitative characterization and they are sufficient to reflect relative activity within the reactors.

In the recycle reactor, initial methane percentage in the generated gas was about 12%. This low percentage was due to the existing acidogenic conditions in the reactor. An increase in the methane concentration as a result of the activity of methanogens was observed during the third stage due to the increase in leachate frequency from two to three times per week together with buffer addition. After the onset of methanogens in the recycle reactor, methane percentage reached 71% at the end of the experiments. On the other hand, high initial methane percentage of 73% in the single pass reactor was observed due to the establishment of methanogenic conditions before. Methane production started decreasing and reached to 51% at the end of the study due to the washout of organic content in system and the loss of the activity of methanogens by the decrease in substrate. Some fluctuations were observed in the decreasing trend due to the loss of sample during the transport.

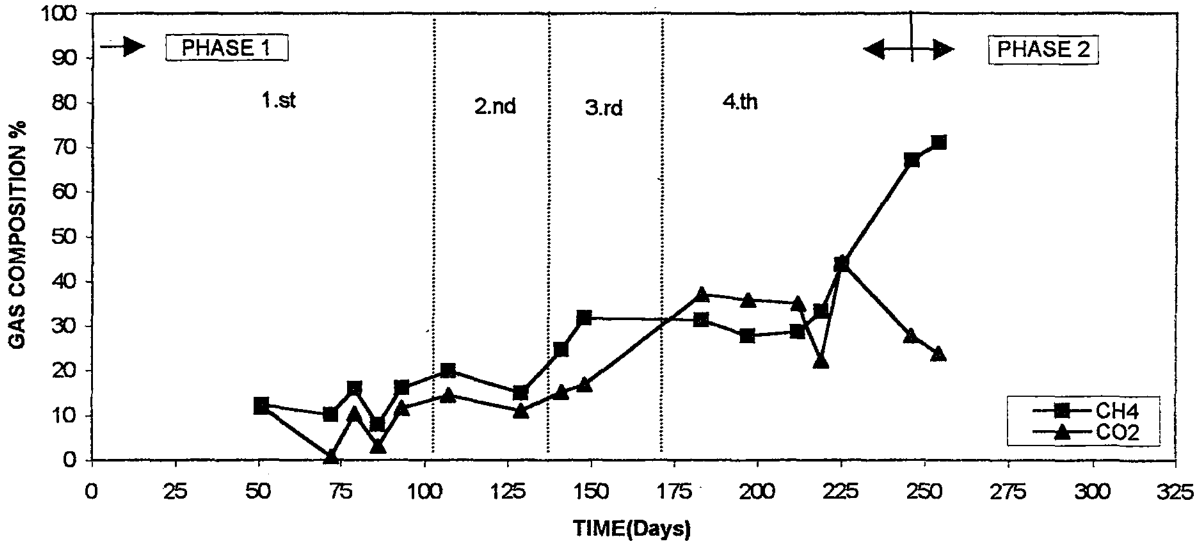


Figure 4.5 Gas Composition from the Recycle Reactor

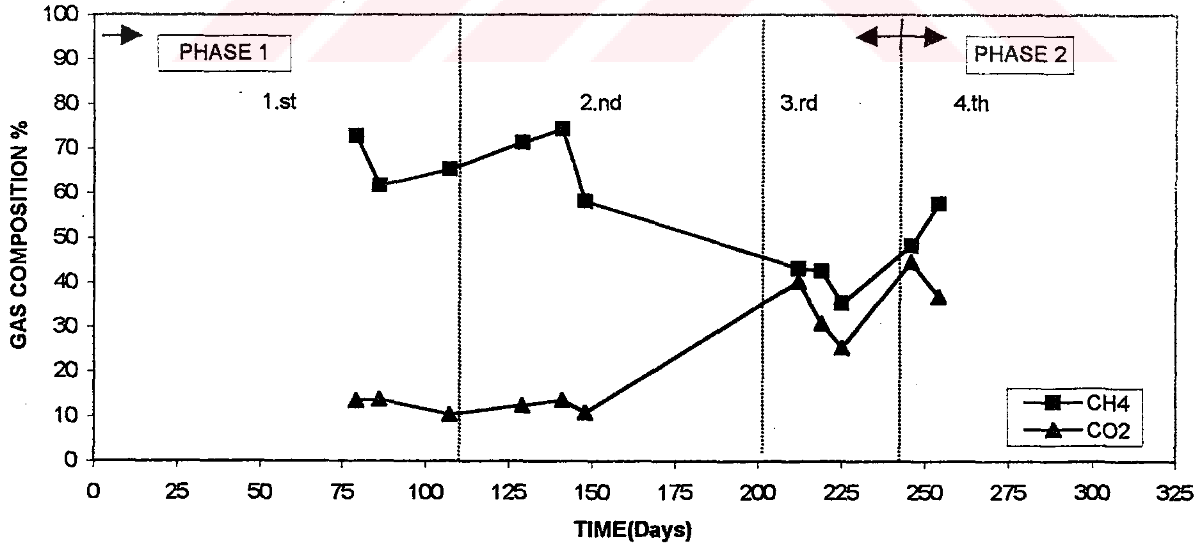


Figure 4.6 Gas Composition from the Single Pass Reactor

Cumulative methane productions were obtained by using daily gas production and gas composition data together. The methane production of days in between two consecutive gas composition analyses was obtained by multiplying the daily gas volume by the average of the methane readings of the two consecutive days. The cumulative methane production of recycle and single pass reactors are displayed in Figures 4.3 and 4.4, respectively. Although the results were inaccurate as a direct consequence of inaccurate cumulative gas readings explained in previous section, they can be used as a useful indicator of reactors behavior. Figures clearly indicate that cumulative methane and carbon dioxide productions were higher in the recycle reactor than in the single pass reactor. Cumulative volume of methane produced in the recycle reactor was 145 L, in the single pass reactor was 125 L. At the same time, in the recycle reactor 101 L of carbon dioxide was produced, while in the single pass reactor only 29 L.

4.2 LEACHATE ANALYSIS

Leachate from simulated landfill reactors was monitored for indicator parameters including COD, pH, alkalinity, phosphate, chloride, ORP, sulfate, sulfide, conductivity and selected heavy metals (Fe, Cu, Cd, Zn, Ni). The results of these analyses are presented in Tables of Appendix B and discussed in the following section.

4.2.1 Chemical Oxygen Demand (COD)

Leachate chemical oxygen demand (COD) was monitored as an indicator of organic strength. Leachate COD concentrations for recycle and single pass reactors are shown in Figure 4.7 and 4.8, respectively.

During Phase 1, at the beginning of the first stage, the COD concentrations of the recycled reactor was about 10,000 mg/L. The application of leachate recirculation in order to enhance the waste stabilization in the reactor by increasing the uniformity of moisture, substrate and nutrient distribution caused a sharp increase in COD values because recirculation was made from the leachate in storage container of the reactor having a high organic content of about 26,000 mg/L. The COD values in the reactor rose from 10,000 mg/L to about 20,855 mg/L at the end of this stage. Although addition of 1N KOH could not provide a decrease in leachate COD due to the high organic content of the recirculated leachate. Buffer addition helped 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 throughout the second stage. COD values in the recycle reactor began to decrease from about 19,206 mg/L on Day 106 to 11,109 mg/L on Day 138 by the leachate recirculation from the container of single pass reactor having low organic content of about 700 mg/L and high buffer capacity. The decrease occurred owing to dilution of the high organic content in the recyle reactor with the leachate from single pass reactor having low COD concentration and introduction of methanogens into the reactor which helped the onset of methanogenic conditions. Moreover, increasing recirculation frequency was also another reason of the decrease in COD concentrations. During the third stage, the increase in the frequency of recirculated leachate from two times per week to three times per week did not affect the conversion rate of organics which was reflected by constant COD concentrations and gas production until the start of the buffer addition. After the addition of Na_2CO_3 along with the recirculation of three times per week, the conversion of organics to methane and carbon dioxide was accelerated rapidly because increased alkalinity in system prevented the accumulation of volatile organic acids and decreased their unwanted effects on methanogens. This rapid decrease continued until the middle of the fourth stage. After Day 200, a significant decrease in COD concentrations was not observed indicating the existence of microbially refractory organics.

In contrast to the recycle reactor, organic strength in the single pass reactor was about 1000 mg/L at the beginning of the first stage in Phase 1 due to the near completion of waste stabilization in the previous research. Most of the readily biodegradable organics were stabilized before the start of this study. Initial decrease in leachate pH, alkalinity and daily gas production proved this nearly completed conversion. The COD concentrations of single pass reactor dropped to almost 511 mg/L on Day 117. Throughout the second stage of operation, the leachate COD concentrations remained constant except daily fluctuations seen after the addition of leachate having high organic content from the recycle reactor in order to prevent substrate deficiency for the growth of methanogens. Moreover, the COD values continued to stay constant along with a slight decrease in the second stage because of insufficient moisture for microbial activity and no washout during the third stage. The COD concentrations were between 358-290 mg/l at this stage.

During Phase 2, after the addition of selected heavy metals, the conversion of waste continued in both reactors until the end of experiments since microorganisms providing decomposition were not inhibited by the added metal concentrations. COD concentrations in the recycle and the single pass reactors decreased from 1309 mg/L on Day 245 to 430 mg/L on Day 307 and from 290 mg /L on Day 245 to 138 mg/L on Day 307, respectively. The conversion of waste was nearly completed in both reactors and remaining COD was mainly due to the presence of refractory organics. While leachate recirculation was the main mechanisms for the removal of organics in the recycle reactor, washout became an important mechanism in the single pass reactor.

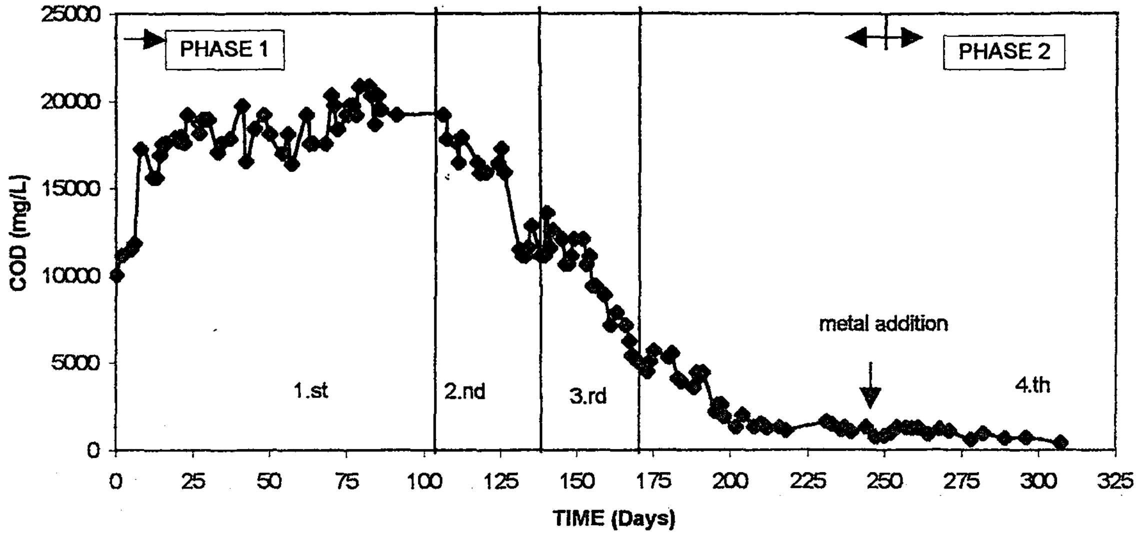


Figure 4.7 Leachate COD concentrations from the Recycle Reactor

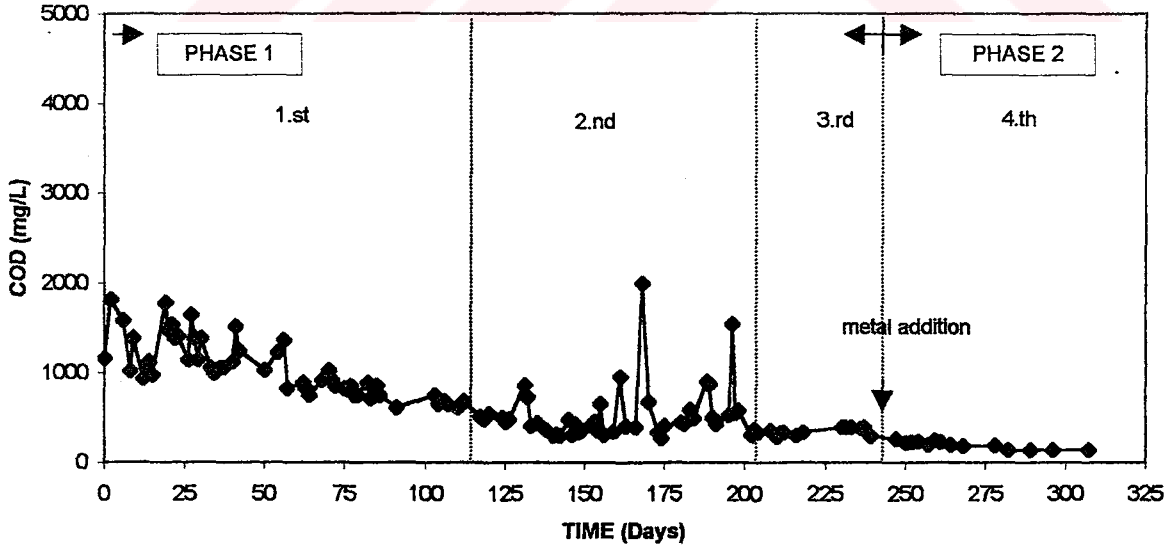


Figure 4.8 Leachate COD concentrations from the Single Pass Reactor

4.2.2 pH

The pH values of reactors were monitored routinely throughout the experimental study due to its 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, acid forming bacteria have an optimum pH range of 5-6. Methane formation will proceed in pH range of 6.5-8.0. The optimum pH for methane generation is between 7.0-7.2.

The change in leachate pH from the reactors is given in Figures 4.9 and 4.10. During the first phase, the initial pH value of the recycle reactor was measured as 5.61 and a slight increase was observed during the first 20 days by the introduction of moisture as 1L leachate recirculation into the reactor. After the Day 20, the pH values begun to decrease because acidogenic conditions in the reactor became more intense by the recirculation of leachate having high organic content and low pH and buffer capacity. To overcome this difficulty and increase the pH of leachate, an attempt was made by the addition of 1N KOH together with leachate recirculation once a week. The pH values rose from 5.62 on Day 56 to 6.04 on Day 86. However, the addition of 1N KOH was stopped on Day 86 because potassium cation reached to inhibitory level of 3000 mg/L. in the reactor. Therefore, a slight decrease in pH values was observed until the beginning of the second stage. The recirculation of leachate from single pass reactor with low organic content and high pH values provided relatively constant pH values at about 6.00 in the recycle reactor. Along with the addition of Na_2CO_3 buffer solution, a sharp increase in pH values was observed on Day 142. The pH values rose from 5.80 to 6.98 on Day 159. After the rapid increase, pH stayed constant until metal addition.

On the other hand, initial pH value in the single pass reactor was about 7.78. Initially high pH values during the first 26 days of stage 1 began to decrease due to nearly completed waste stabilization and washout of bicarbonate, carbonate ions providing alkalinity to the system. Although a slight increase was observed at the end of the third stage, the pH values of single pass reactor stayed a at constant value of approximately 6.90 throughout the first phase of the experiment.

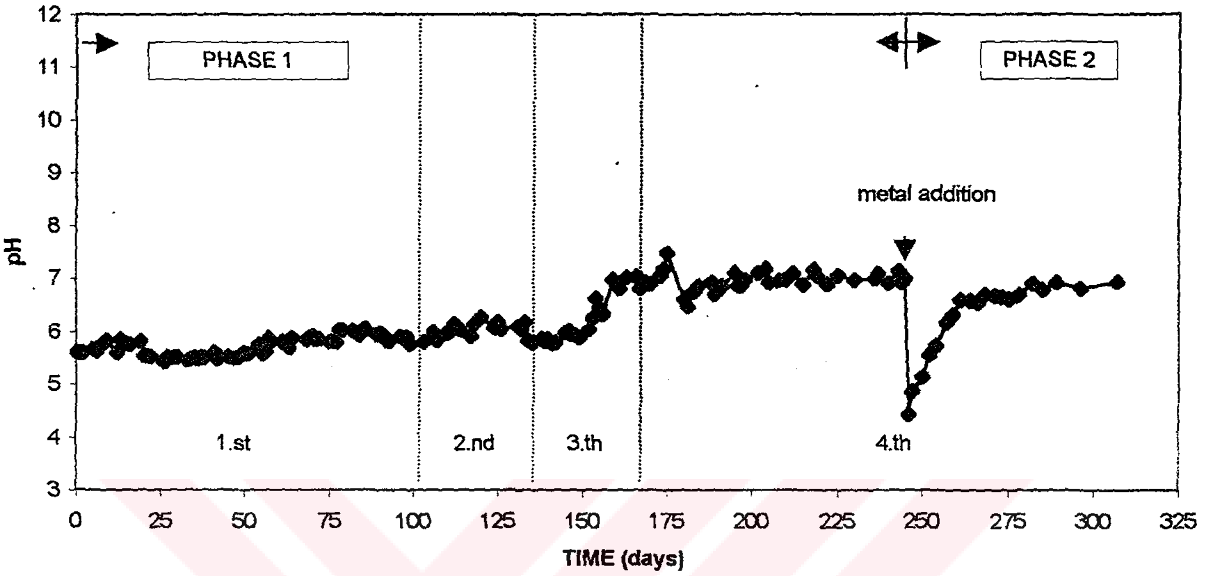


Figure 4.9 Leachate pH from the Recycle Reactor

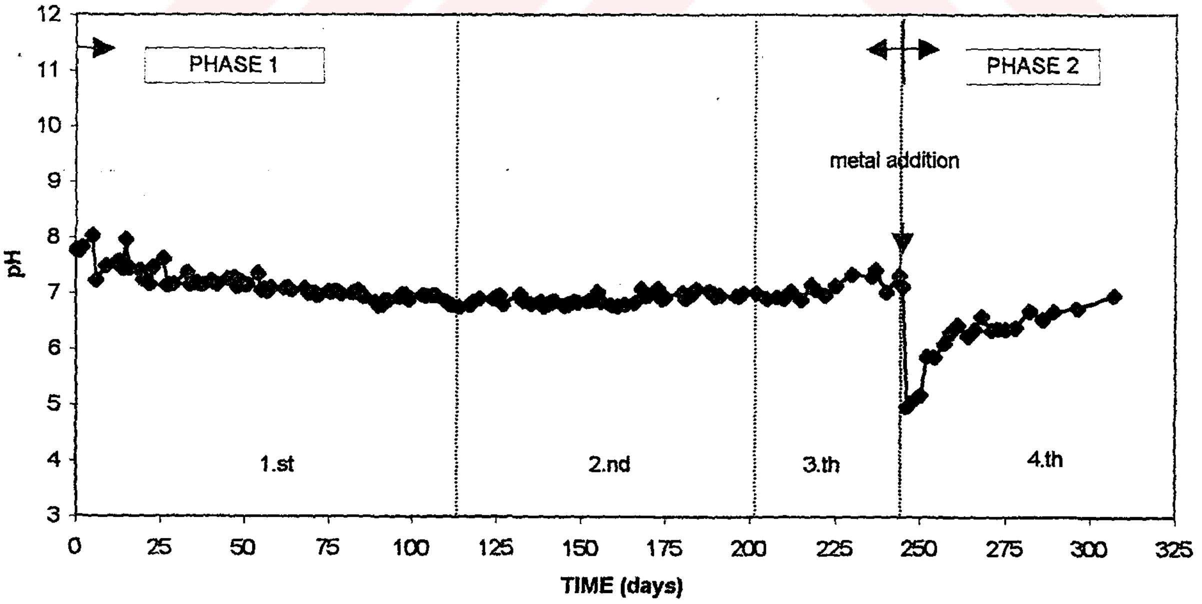


Figure 4.10 Leachate pH from the Single Pass Reactor

Along with the metal addition, the pH values of the recycle reactor and the single pass reactor decreased from the neutral pH values in both reactor to 4.43 and 4.98, respectively. The decrease in pH values is primarily due to the addition of metal solution having acidic properties and precipitation of CO_3 ions contributing to alkalinity. After the establishment of sulfate-sulfide equilibrium in the reactors, the precipitation of heavy metals was controlled by sulfide and the pH of recycle reactor and single pass reactor rose to 6.93 and 6.98, respectively.

4.2.3 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. The alkalinity of the system is reflected by the association of cations and anions present in the system including volatile acids, ammonium, calcium, magnesium and sodium. The presence of a buffer capacity in system is very important for the continuity of biological stabilization processes. The measured alkalinity concentrations for the recycle reactor and the single pass reactor are given in Figures 4.11 and 4.12, respectively.

Initial alkalinity concentration in the recycle reactor was 2493 mg/L as $CaCO_3$. After Day 20, a decline in the alkalinity similar to the decrease in pH was observed due to the recirculation of leachate having high organic content and low buffer capacity. The buffer addition on Day 56 increased the alkalinity of system to 3100 mg/L as $CaCO_3$ towards the end of the first stage of recycle reactor. Because potassium cation reached to inhibitory level of 3000 mg/L in system, 1N KOH addition was stopped on Day 84. After stopping the buffer addition, no important change in alkalinity concentrations was observed except a slight decrease in the second stage. A sharp decrease in alkalinity was observed at the beginning of third stage although recirculation frequency increased three times per week. Alkalinity declined to 2020 mg/L as $CaCO_3$ on Day 145. However, the addition Na_2CO_3 enhanced buffer capacity in the reactor and alkalinity increased 2946 mg/L as $CaCO_3$. After the onset of desired conditions alkalinity in the recycle reactor stayed constant until the metal addition phase.

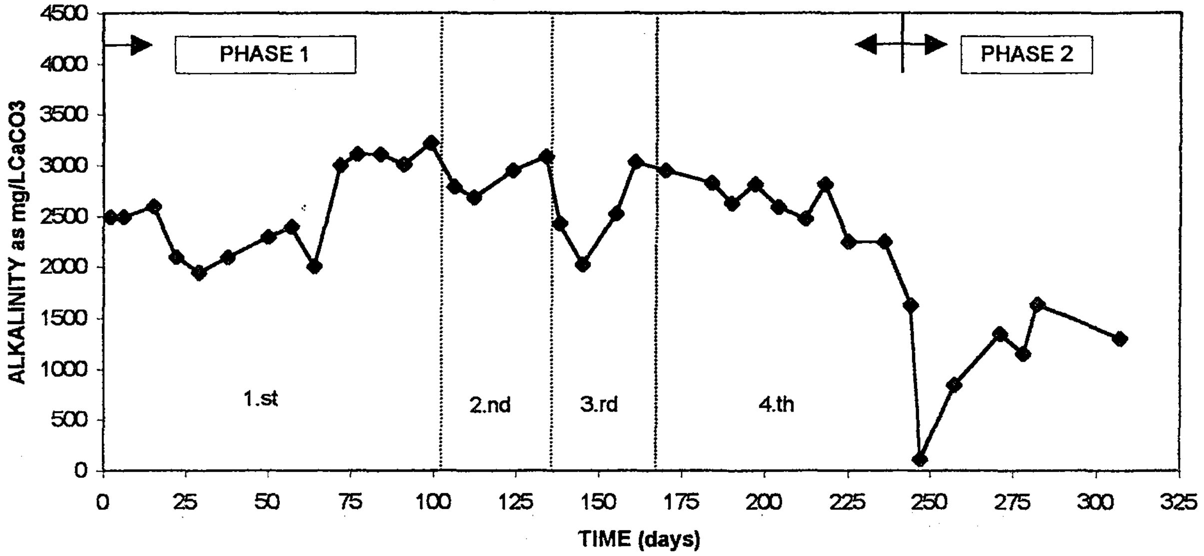


Figure 4.11 Leachate Alkalinity Concentrations from the Recycle Reactor

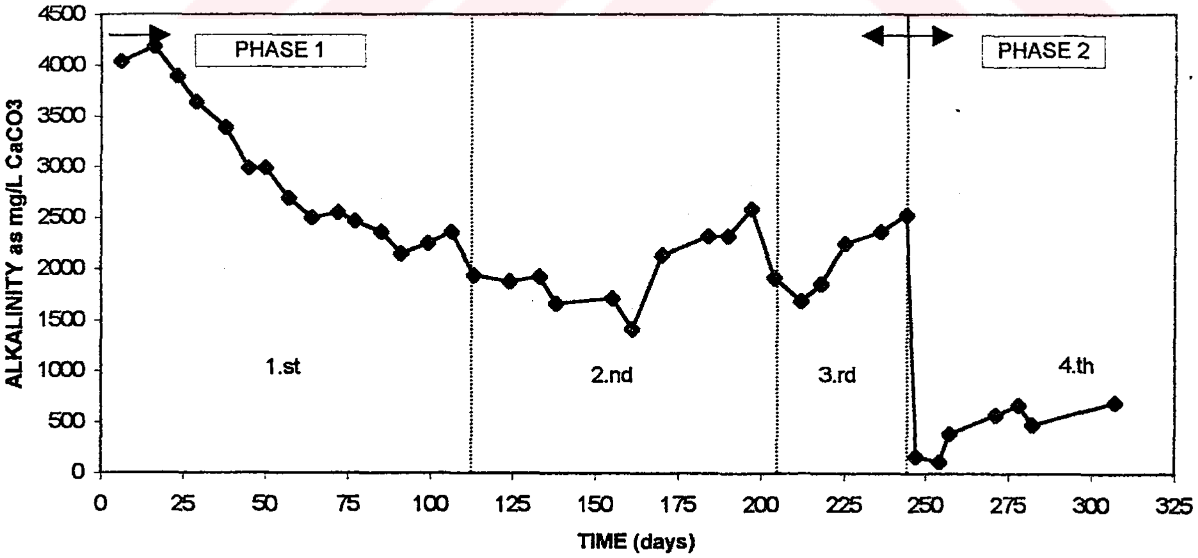


Figure 4.12 Leachate Alkalinity Concentrations from the Single Pass Reactor

On the other hand, in the single pass reactor initial alkalinity was about 4000 mg/L $CaCO_3$. As indicated in Figure 4.12, alkalinity of single pass reactor decreased rapidly due to the washout mechanism occurred in the first stage. Along with an initial decrease, alkalinity increased in the middle of second stage as a result of provided alkalinity from the recycle reactor and it reached to 2531 mg/L as $CaCO_3$ at the end of the first phase.

During the second stage, after the metal addition, alkalinity concentrations declined nearly zero since $CO_3^{=}$ anions providing alkalinity were precipitated with heavy metals. Initially, insufficient sulfide concentrations resulted in this precipitation. Along with reduction of sulfate to sulfide to form metal-sulfides, $CO_3^{=}$ anions in both reactor became free and alkalinity increased at the end of experiments. However, the increase in the alkalinity of recycle reactor was more clear due to enhancement of sulfate reduction by leachate recirculation.

4.2.3 Orthophosphate

Orthophosphate was monitored as one of the major nutrients required in the anaerobic degradation. The daily variations in concentrations of orthophosphate observed during the experimental period are presented in Figures 4.13 and 4.14

The initial concentration of orthophosphate in recycle reactor was 171 mg/L. The orthophosphate concentrations in leachate, increased to approximately 226 mg/L due to the leachate recirculation that was made from the storage container of the reactor having a high orthophosphate concentration of about 285 mg/L. However, towards the middle of the first stage, orthophosphate concentrations started to decrease as a result of the enhancement of the utilization of orthophosphate by microorganisms and the dilution caused by water additions and the sharp decrease continued until the end of the third stage. The leachate phosphate concentration reached to 25 mg/L at the beginning of the fourth stage. The orthophosphate concentrations stayed approximately constant during that period lasted until the metal addition. On the other hand, the orthophosphate concentrations in the single pass reactor decreased from 56 to 39 mg/L due to washout mechanism at the end of first stage and the slight decrease continued until the middle of second stage. Along with

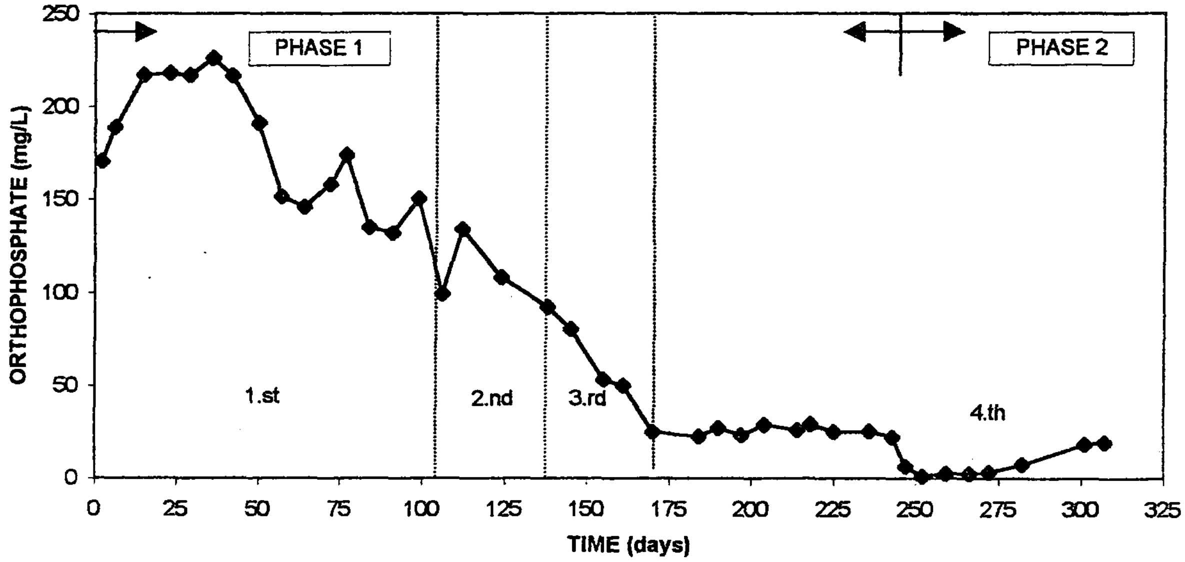


Figure 4.13 Leachate Orthophosphate Concentrations from the Recycle Reactor

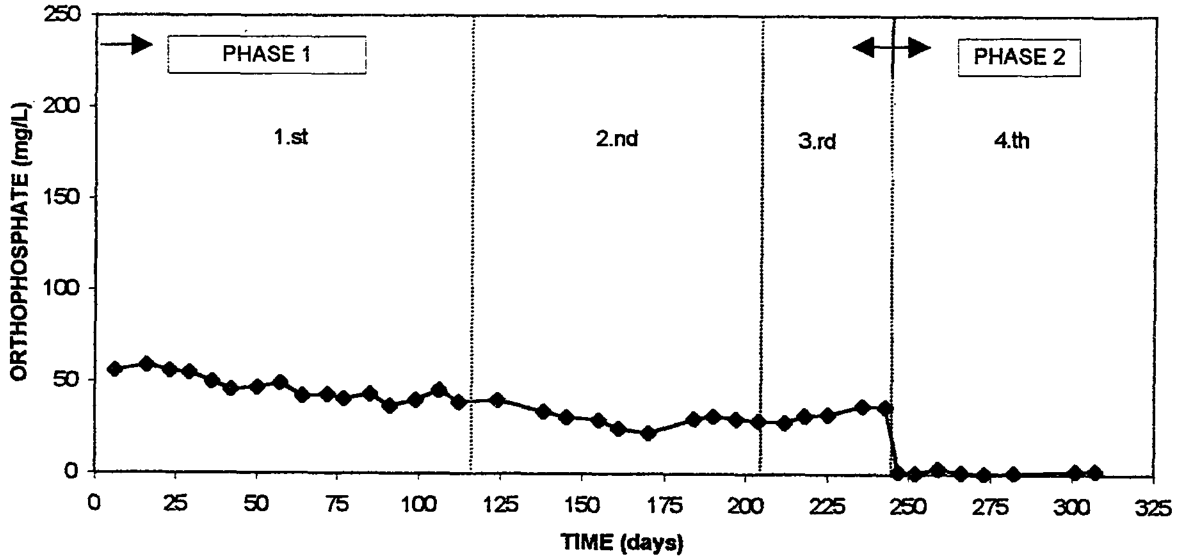


Figure 4.14 Leachate Orthophosphate Concentrations from the Single Pass Reactor

the addition of leachate having high organic content, a slight increase in orthophosphate concentrations was observed as result of hydrolysis of organic and polyphosphates. The orthophosphate concentration reached to 37 mg/L before the addition of the selected heavy metals.

During the Phase 2, the initial concentration of orthophosphate in both reactors was found to be similar indicating the uniformity in both reactors. The concentrations for recycle reactor and single pass reactor were 22 and 37 mg/L, respectively. After the addition of the salts of the selected heavy metal ions, a sharp decrease in orthophosphate concentrations was observed in both reactors as a result of precipitation with the selected heavy metals. Toward the end of experiment, an increase in the recycle reactor was observed due to reduction of sulfate to sulfide to form insoluble metal sulfides. On the other hand, there is no change in the orthophosphate concentrations of single pass reactor due to washout of sulfate and insoluble orthophosphates.

4.2.5 Chloride

Chloride was monitored as a conservative tracer in order to estimate the dilution and evaporation effects throughout the experiments. Chloride concentrations for the recycle reactor and the single pass reactor are presented in Figures 4.15 and 4.16.

Leachate chloride concentrations in the recycle reactor decreased at the beginning and increased slowly with some fluctuations throughout the first phase due to the recirculation of leachate with higher chloride concentrations from the container. Chloride concentration of the reactor stayed constant between Day 103 and Day 170. After the Day 170, leachate chloride decreased slowly due to the dilution effect of water. Initial chloride concentration of single pass reactor and the recycle were approximately 371 mg/L. In contrast to the recycle reactor, the chloride concentration of the single pass reactor dramatically decreased during the first stage due to the washout. After the first stage, chloride concentrations stayed constant except the high chloride value measured on Day 161 reflecting the effect of direct recirculation of leachate having high chloride content from the recycle reactor.

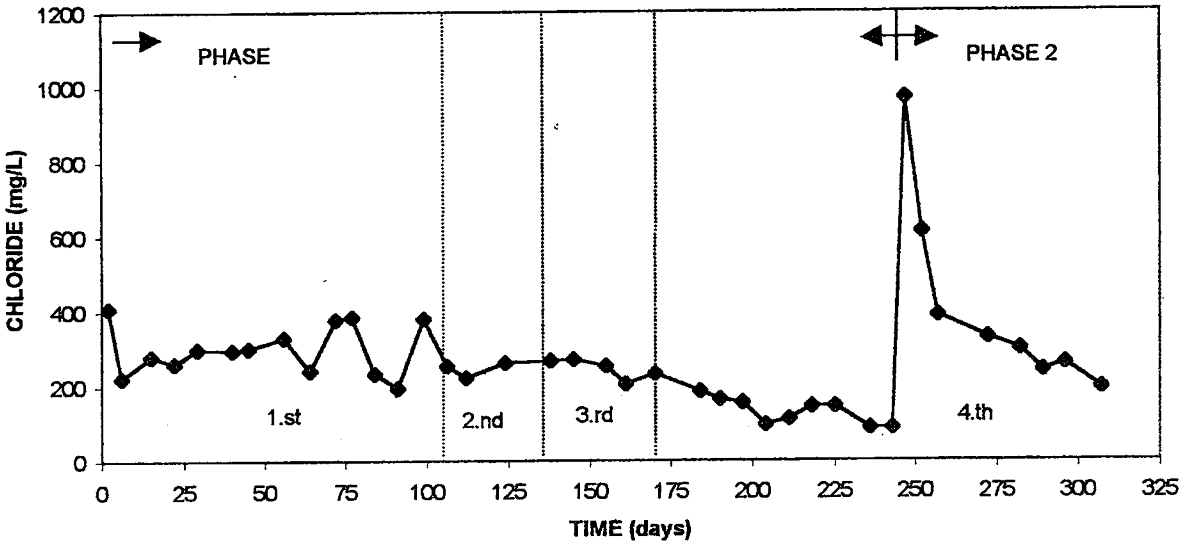


Figure 4.15 Leachate Chloride Concentrations from the Recycle Reactor

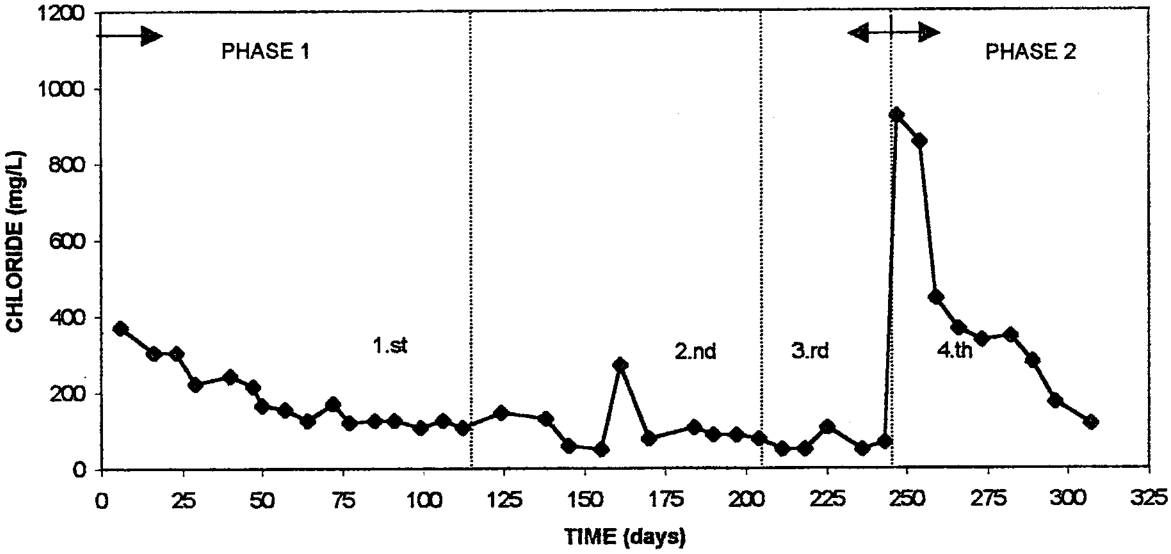


Figure 4.16 Leachate Chloride Concentrations from the Single Pass Reactor

Along with the addition of metal solution into the reactors, chloride concentrations of recycle and single pass reactors increased to 971 and 923 mg/L respectively due to the chloride salts of the added metals such as $FeCl_3$. After the sudden increase in chloride concentration in both reactor, a sharp decrease was observed as a result of washout. As indicated in Figures 4.15 and 4.16, the dilution effects in the single pass reactor was higher than the recycle reactor.

4.2.6 Oxidation-Reduction Potential (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 and limited access to atmospheric oxygen. Measured ORP values for recycle and single pass reactors are presented in Figure 4.17 and 4.18.

Initial ORP values in the recycle reactor were positive because of the unsuitable sampling procedures and the initial presence of oxygen in the reactor. However, reducing conditions were established by Day 30 and ORP values decreased to –120 mV. While solid waste decomposition proceeded, ORP values of recycle reactor began to be more negative as a result of the establishment of the methanogenic conditions. During the second stage, ORP values in the recycle reactor were still around –150 mV with a wide fluctuations from Day 103 to Day 135. At the end of the second stage, the ORP values measured were not reliable due to insensitivity of ORP probe. The measurement of ORP values was stopped until the maintenance of the probe. After the probe was conditioned before use, the measurement of ORP restarted on Day 189. Gradual decline in ORP values continued with an average of about –200 mV until the metal addition. During the same period, ORP values in the single pass reactor ranged between –70 mV to-305 mV. ORP values of single pass reactor were more negative than those in the recycle reactor during Phase 1 because methanogenic conditions in the single pass reactor were established earlier than the recycle reactor. As mentioned above, ORP values of the single pass reactor was not monitored between Day 138 and 189 due to the analytical problems.

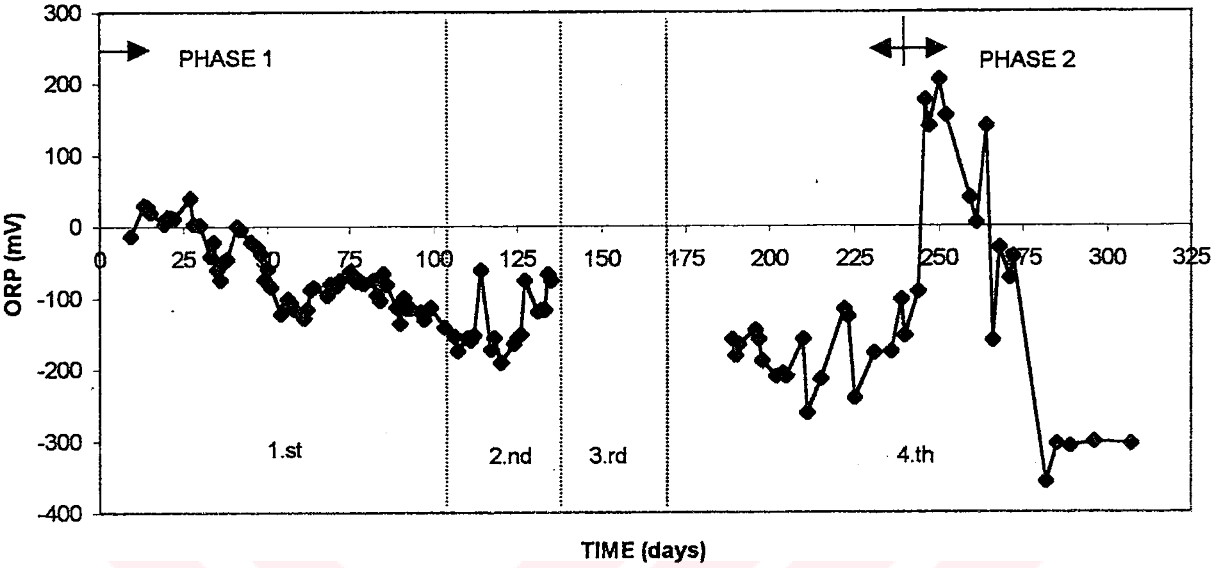


Figure 4.17 Leachate ORP Concentrations from the Recyle Reactor

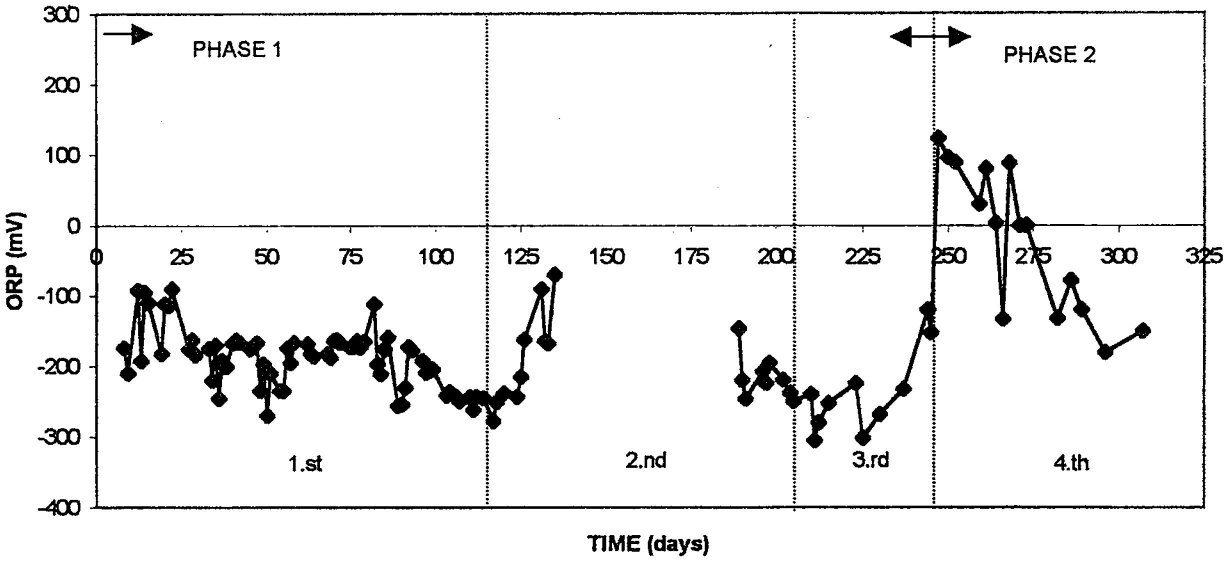


Figure 4.18 Leachate ORP Concentrations from the Single Pass Reactor

During Phase 2, dissolved metal salts in one liter deionized water were introduced into the reactors and ORP values became immediately positive due to the presence of oxidized forms of metal such as Fe^{+3} and the presence of sulfates in the metal salts. ORP values of the recycle reactor and the single pass reactor were 177 mV and 123 mV on Day 246, respectively. The transition from the oxidizing due to metal addition to reducing conditions on Day 266 in the recycle reactor and on Day 282 in the single pass reactors was provided by the active methane fermentation and the formation of sulfide from sulfate respectively. The ORP values of the recycle reactor was more negative than those in the single pass reactor towards the end of experiments because leachate recirculation enhanced the reduction of sulfate to sulfide.

4.2.7 Sulfate and Sulfide

Sulfates and sulfides were monitored as a good 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 concentrations for recycle and single pass reactors are presented Figures 4.19 and 4.20, respectively. Sulfide concentrations for recycle and single pass reactors are presented Figures 4.21 and 4.22, respectively.

During Phase 1, since highly reducing conditions confirmed by negative ORP values were established in both reactors before, sulfate concentrations were not observed except once or twice. In the recycle reactor, sulfate concentrations reached to 185 mg/L throughout the first stage because of recirculation of leachate from the recycle container having high sulfate concentration and initial oxygen in system. On the other hand sulfate concentration in the single pass reactor reached to 750 mg/L at the beginning of third stage because last organic matter addition by leachate recirculation was made from inside of its own container having high sulfate concentration. The high sulfate concentration in the reactor decreased to zero on Day 240 due to the reduction of sulfate to sulfide and washout.

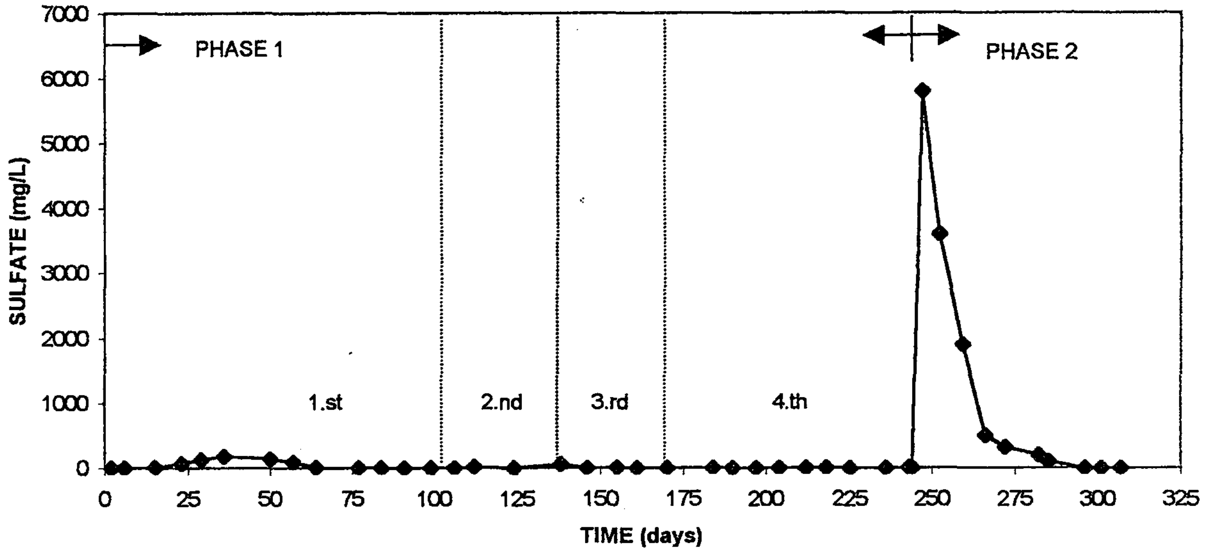


Figure 4.19 Leachate Sulfate Concentrations from the Recycle Reactor

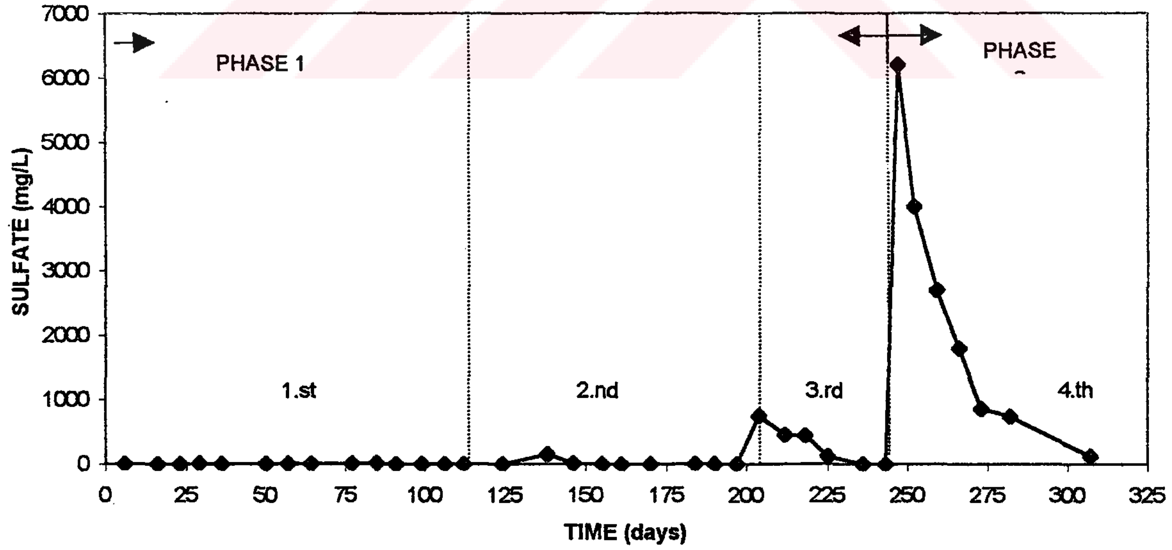


Figure 4.20 Leachate Sulfate Concentrations from the Single Pass Reactor

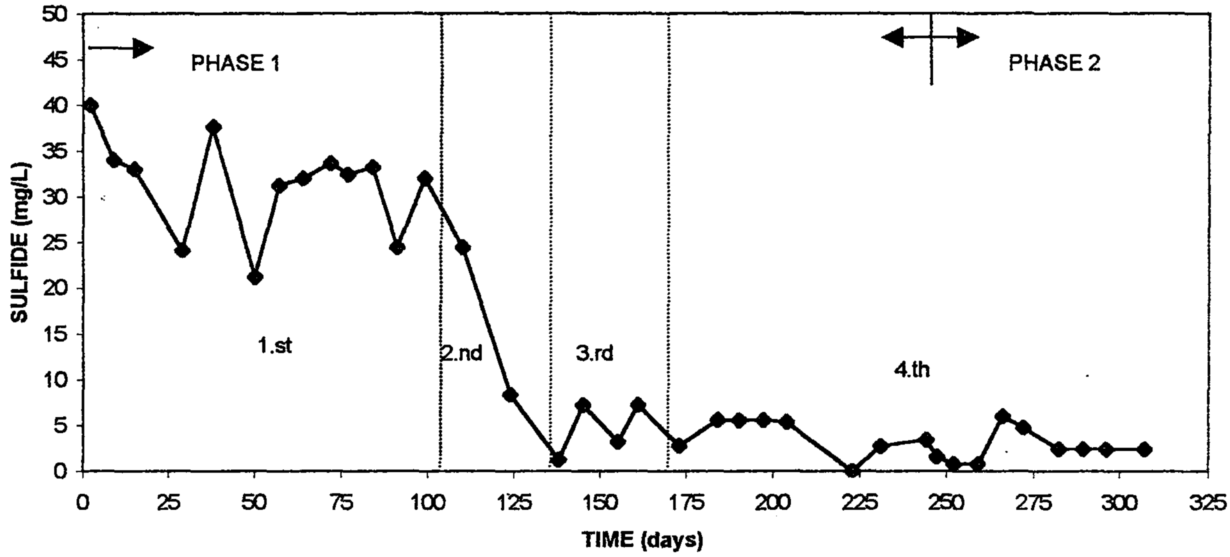


Figure 4.21 Leachate Sulfide Concentrations from the Recycle Reactor

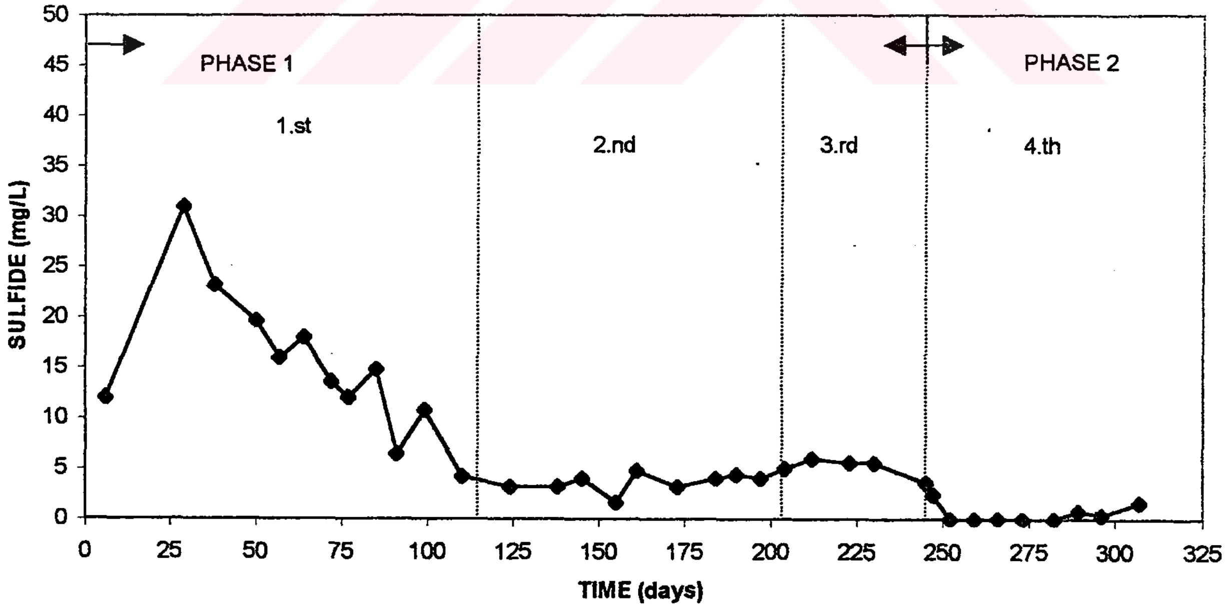


Figure 4.22 Leachate Sulfide Concentrations from the Single Pass Reactor

Initial sulfide concentration in the recycle reactor was about 40 mg/L. While a slight decrease in the first stage of the recycle reactor was observed due to precipitation, a sharp decrease in the second stage of the recycle reactor was monitored as a result of recirculation from single pass container having low sulfide at or below 5 mg/L in leachate through the concentration. After this decline, average sulfide concentrations were about 5 mg/L until the second phase. On the other hand, sulfide concentrations in single pass reactor were lower and removed rapidly from leachate by precipitation and washout mechanisms in the first stage. After this stage, sulfide concentrations remained second and third stage.

During Phase 2, sulfate concentration increased immediately in both reactors because the metal sulfates except zinc were used to understand precipitation mechanisms of metals together with sulfide compounds. The sulfate concentrations of recycle reactor and single pass reactor were 5800 and 6200 mg/L on Day 247, respectively. As indicated in Figures 4.19 and 4.20, sulfate concentrations were reduced rapidly to sulfides. While all sulfate concentrations in recycle reactor reached zero on Day 296 due to leachate recirculation, sulfate concentration in the single pass reactor were 125 mg/L at the end of experiments. On the other hand, formed sulfides from sulfate reduction precipitated with heavy metals and after precipitation, remaining sulfides were observed in recycle and single pass reactors as 2.4 mg/L and 1.6 mg/L on Day 307, respectively.

4.2.8 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 recycle and single pass reactors are shown in Figure 4.23.

In both reactor, after the addition of ionic contributions originating with the metal salts the change in leachate conductivity by time followed the same trend; high initial values (11680 µmho/cm in the recycle reactor and 10850 µmho/cm in the single pass reactor) were followed by steady decrease to minimum values 75-81% of the initial values after 62 days. 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 consequenced by anaerobic biological activity. The subsequent precipitation of sulfide as heavy metal sulfides would tend to withdraw significant ionic strength from solution.

In this study, ionic strength was estimated on the basis of the empirical linear approximation

M= Ionic Strength = 1.6×10^{-5} x Conductivity in µmho (Snoeyink and Jenkins, 1980).

The values of the ionic strength as a function of time are presented in Figure 4.24 Since activity is a function of ionic strength, computation of activity coefficients depends on a knowledge of the ionic strength of the medium involved. Activity coefficients were computed for mono-, di- and trivalent ions are presented in Figure 4.25 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, 1987a).

- For ionic strength of more than approximately 0.1

$$-\log \gamma = \frac{0.5 x Z^2 x \mu^{1/2}}{1+\mu^{1/2}} - 0.2\,\mu$$

- For ionic strength of more less approximately 0.1

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

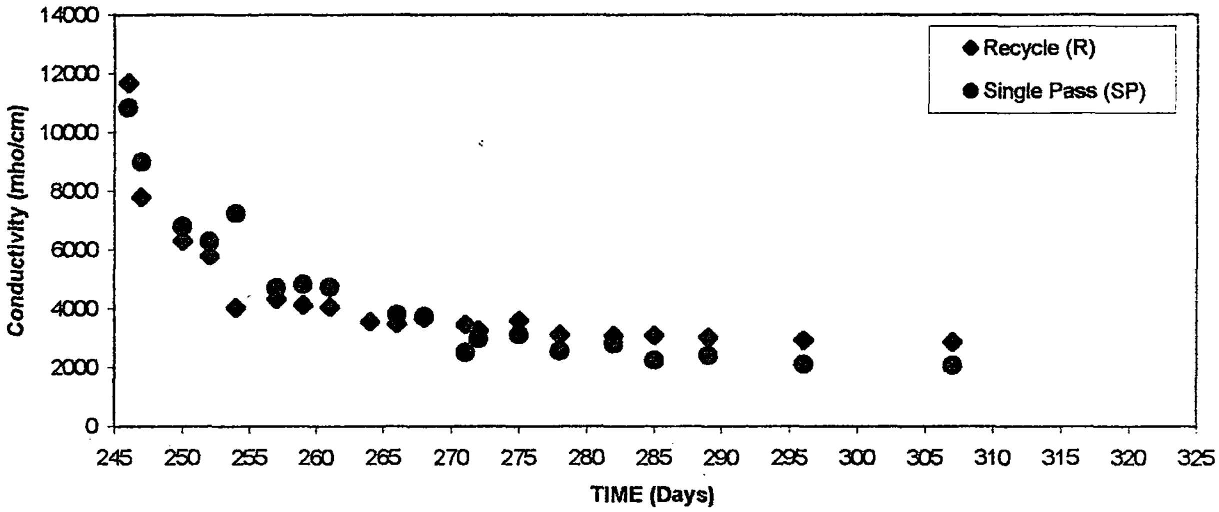


Figure 4.23 Leachate Conductivity from the Recycle and Single Pass Reactors

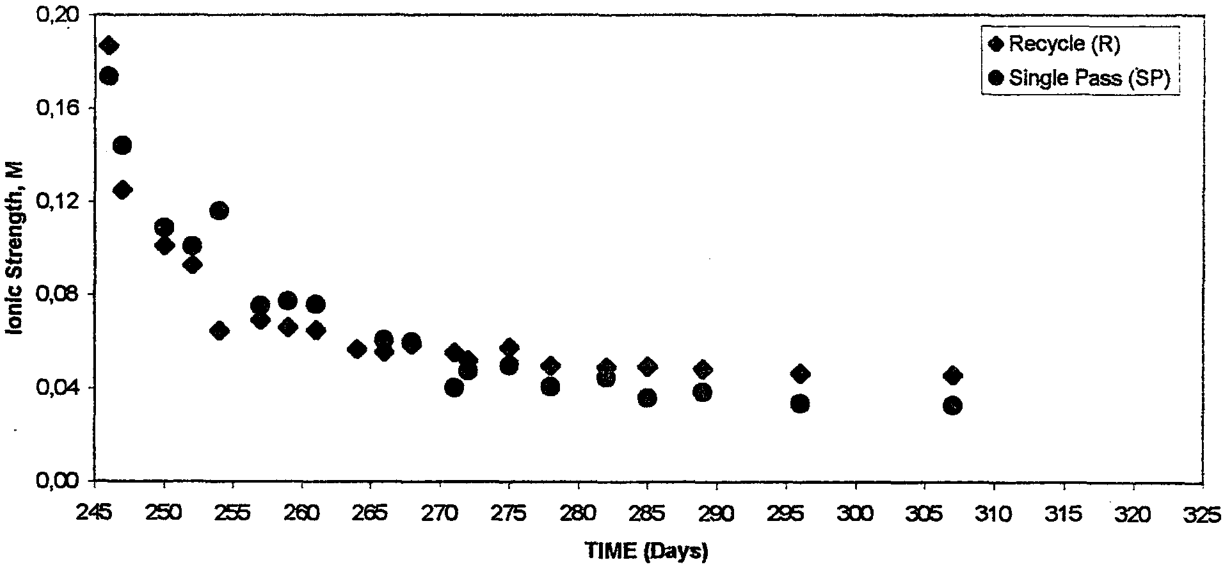


Figure 4.24 Ionic Strength from the Recycle and Single Pass Reactors

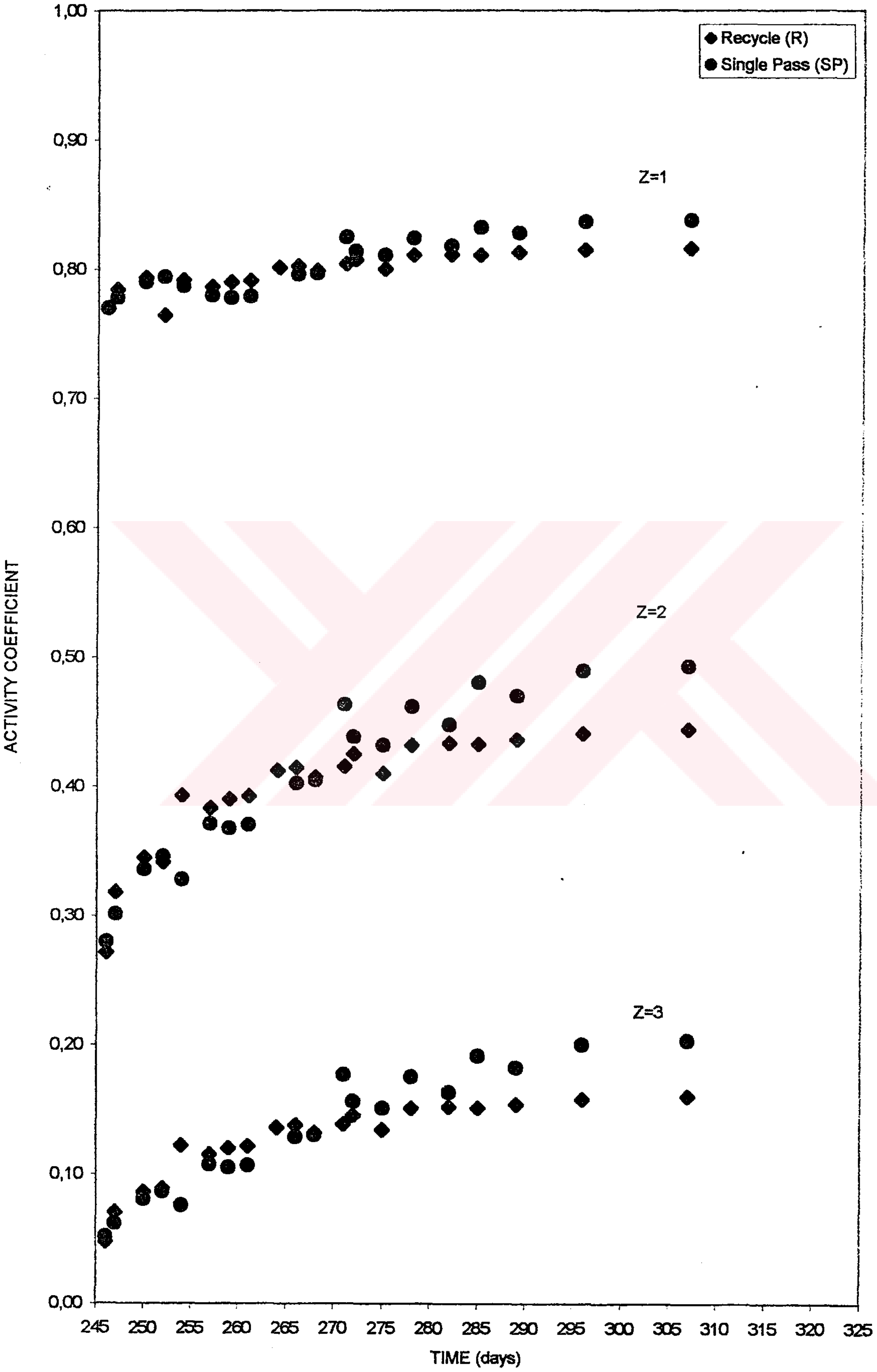


Figure 2.25 Activity Coefficients for Recycle and Single Pass Reactors

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

For monovalent ions such as Na^+, K^+, Cl^- the value of γ averaged 0.79 units for recycle reactor and 0.80 units for single pass reactor. Divalent ions such as Ca^{+2}, Ni^{+2}, Cd^{+2}, Zn^{+2} and SO_4^{-2} had γ values which averaged 0.39 units for recycle reactor and 0.40 units for single pass reactor. 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 0.12 units and 0.13 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.

4.2.9 The Selected Heavy Metals

The behavior and fate of the heavy metals in the terms of their mobility in the reactors under the methanogenic conditions received major attention in this study. The variations in the leachate concentrations and masses of iron, copper, cadmium, nickel and zinc are shown in Figures 4.26 through 4.35. The masses of these metals for recycle and single pass reactors were calculated during leachate recirculation and simulated rainfall addition, respectively.

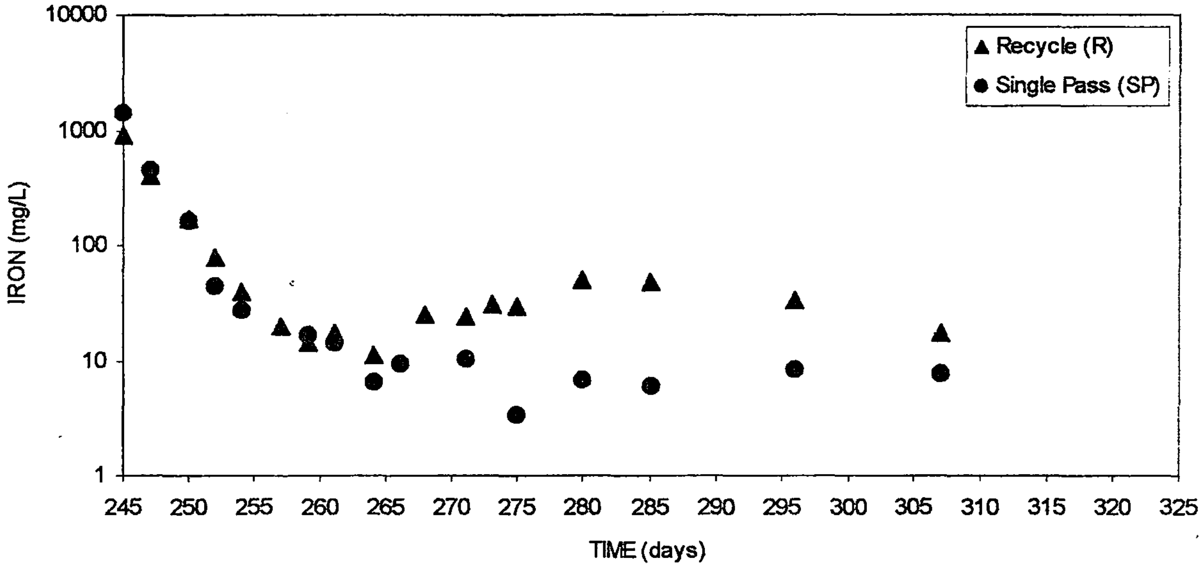
Before co-disposal, the selected metals were monitored several times and insignificant background metal concentrations in the both reactors were found. Along with co-disposal, the selected metals were monitored continuously until the end of the experiments. The selected metals (Fe, Cu, Cd, Ni, Zn) were prepared by dissolving the metal-sulfate salts except zinc in one liter deionized water and loaded into the reactors as stoichometrically equivalent amounts calculated according to the Regulation on Day 245. The calculated masses of iron, copper, cadmium, nickel and zinc for loading in both reactors were 2600 mg, 1300 mg, 130 mg, 1300 mg and 1300 mg, respectively. However, the actual initial masses loaded into the recycle and single pass reactors were measured as 2317 mg and 2374 mg for iron, 1094 mg and 1093 mg for copper, 105 mg and 103 mg for cadmium, 1461 mg and 1490 mg for nickel, 1067 mg and 856 mg for zinc, respectively.

In general, as indicated in Figures 4.26 through 4.35, about 90% of all heavy metals removed from the reactors within the first 10 days due to the establishment of highly reducing environment and the formation of sulfide from sulfate which was providing heavy metal precipitation. The measurements of ORP, sulfate, sulfide and conductivity confirmed the removal of the heavy metals during this period.

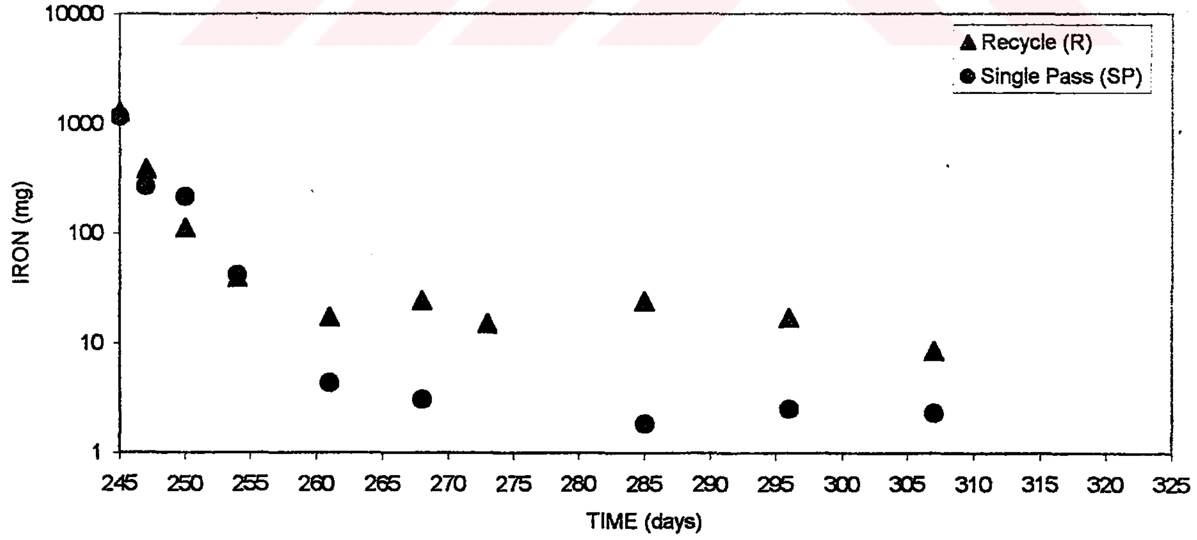
Iron was loaded into the reactors in both forms (Fe^{+3} and Fe^{+2}). However, Fe^{+3} ions reduced to Fe^{+2} species in the reactors due to the existence of reducing conditions. Initial leachate iron concentrations of recycle and single pass reactor were 905 and 1436 mg/L, respectively. Approximately 45% of iron in the recycle reactor and 52% of iron in the single pass reactor were removed in the first day of operation. The decline in concentration of iron was attributed to the effect of washout and the presence of sulfides with subsequent precipitation of iron in both reactors. The impact of sulfide in the recycle reactor was more apparent.

The first day removal of cadmium, nickel and zinc were lower than the other metals. The removal efficiency ranged between 33% - 47% for these metals. All these three metals existed in the reduced form in both reactors.Therefore, the initial high concentrations of these metals were first removed by existing other anions such as carbonate, phosphate and then, along with the onset of sulfide generation, these anions bound with heavy metals were separated and free heavy metals formed insoluble metal-sulfide precipitates. This was confirmed by the measurements of alkalinity, orthophosphate and sulfide, especially in the recycle reactor. On the other hand, in the single pass reactor the primary removal mechanism was the leachate washout.

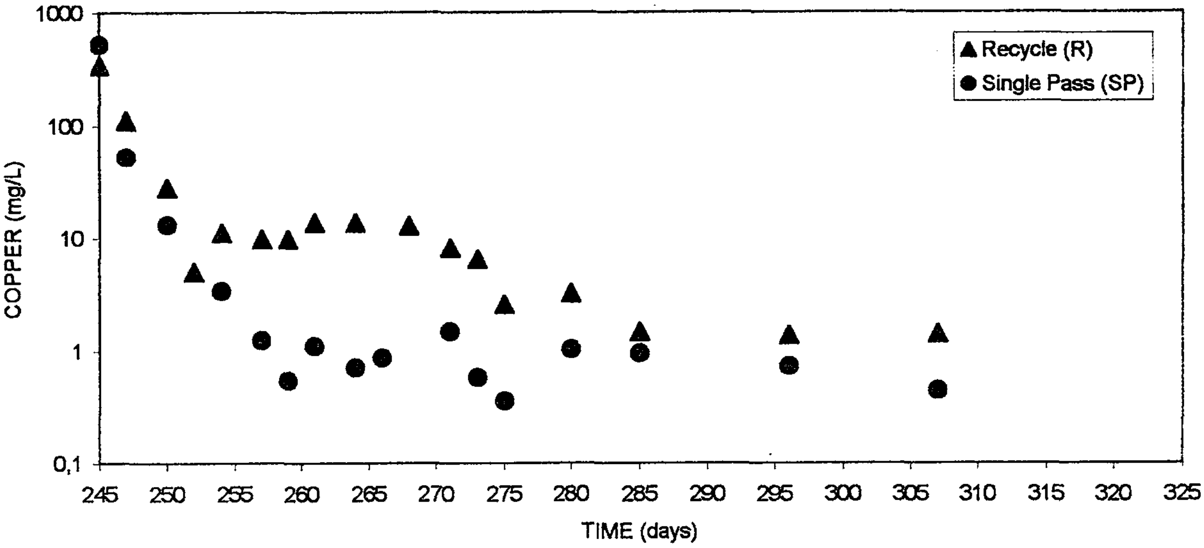
The removal efficiency of copper in the reactors was much more higher than the other metals during the experiments. The first day removal efficiency of copper in recycle and single pass reactors were 56% and 62%, respectively. Copper concentration rapidly decreased in correspondence with the reduction of sulfate to sulfide. Sulfide is known to be a very potent precipitant for copper and form less soluble copper sulfides (pK_{so}=44.1) (Scheinberg, 1991).



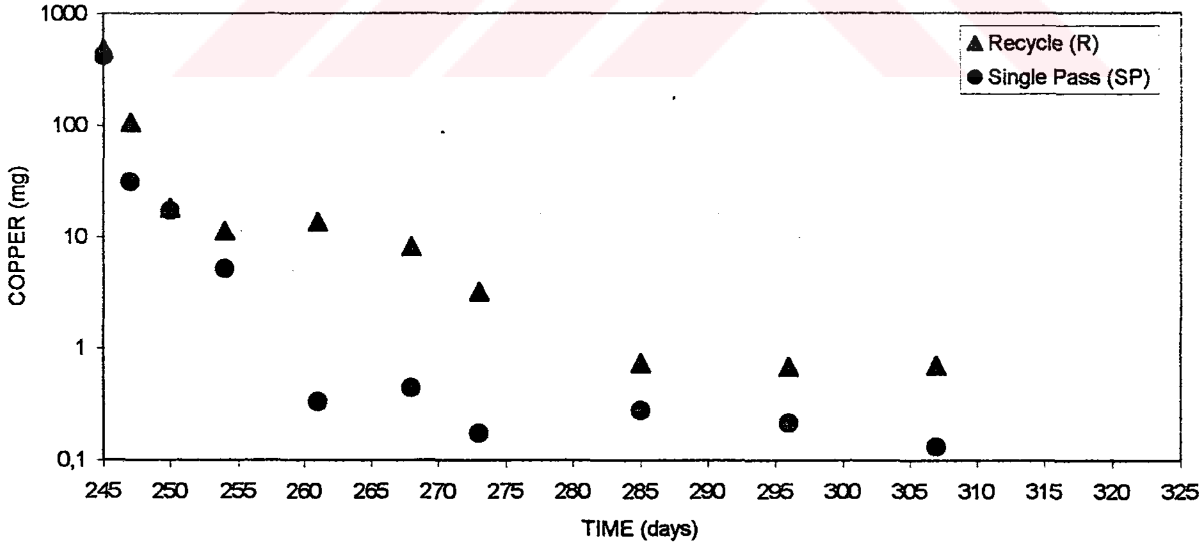
4.26 Leachate Iron Concentrations from the Recycle and Single Pass Reactors



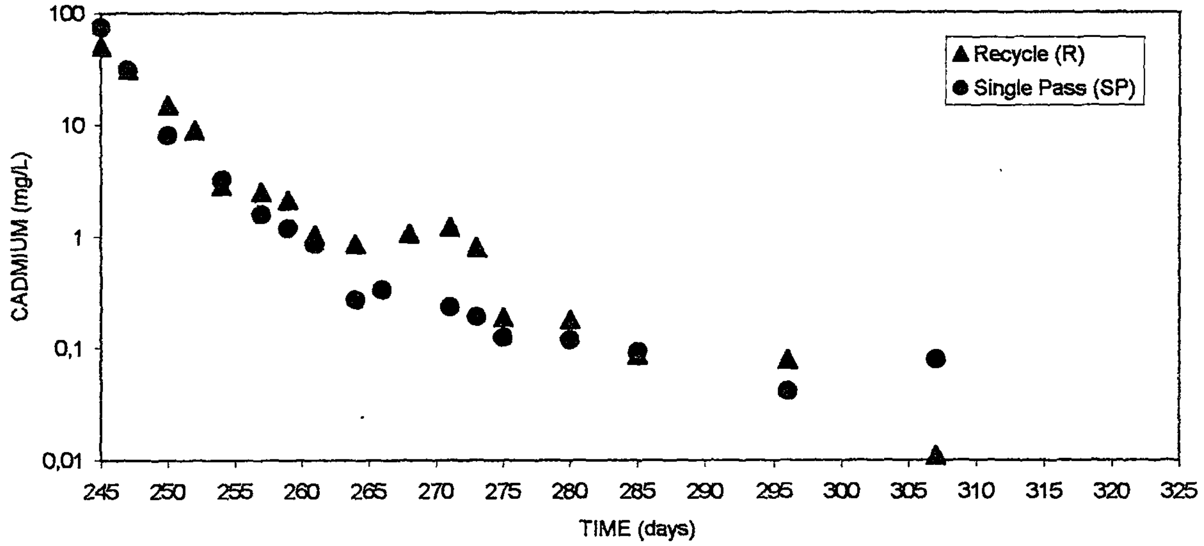
4.27 Leachate Iron Masses from the Recycle and Single Pass Reactors



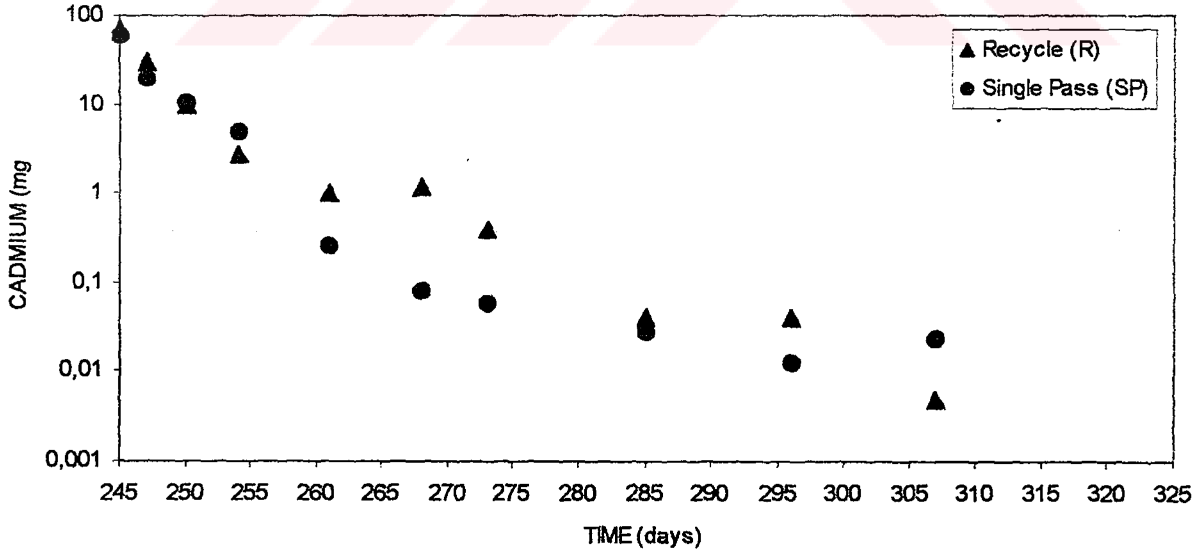
4.28 Leachate Copper Concentrations from the Recycle and Single Pass Reactors



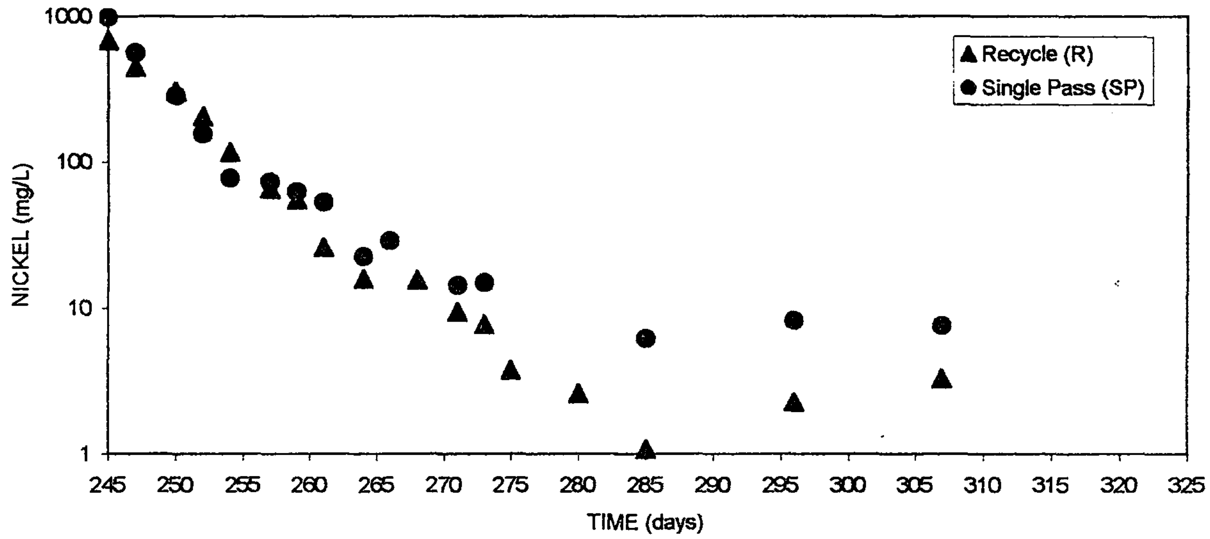
4.29 Leachate Copper Masses from the Recycle and Single Pass Reactors



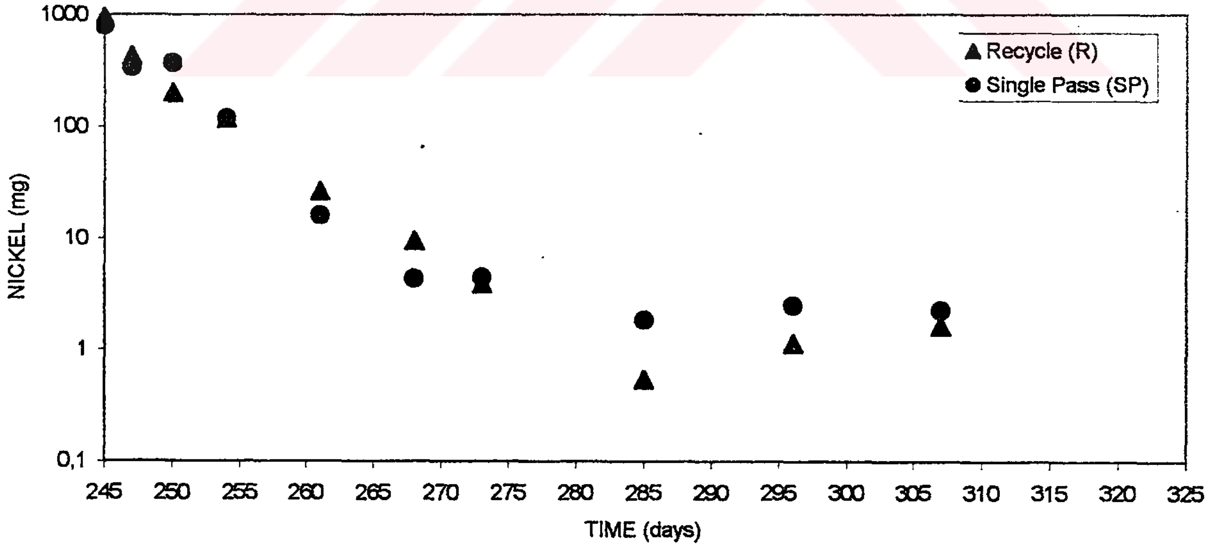
4.30 Leachate Cadmium Concentrations from the Recycle and Single Pass Reactors



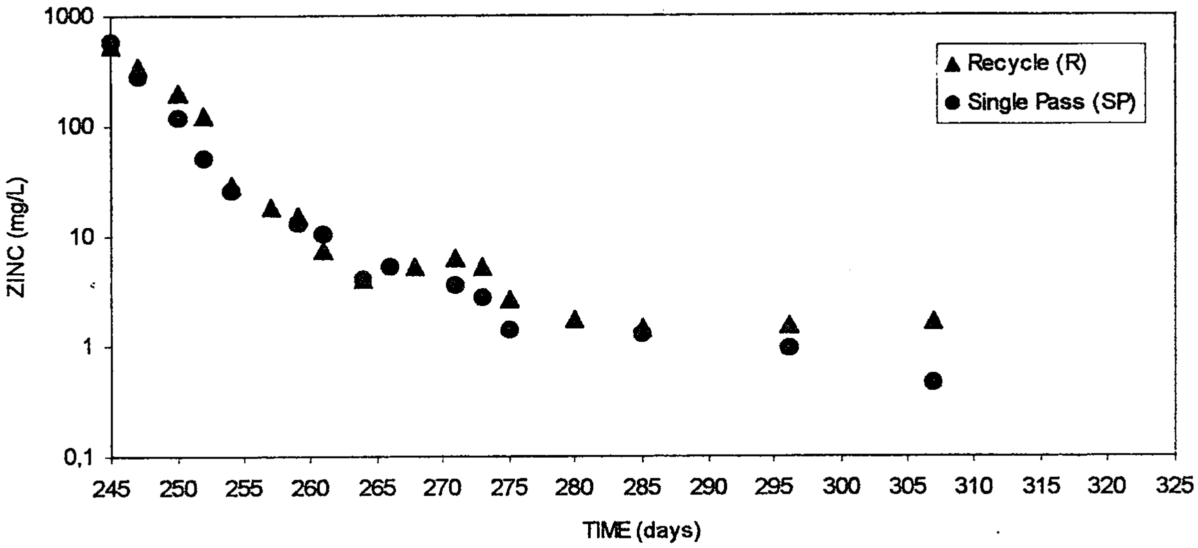
4.31 Leachate Cadmium Masses from the Recycle and Single Pass Reactors



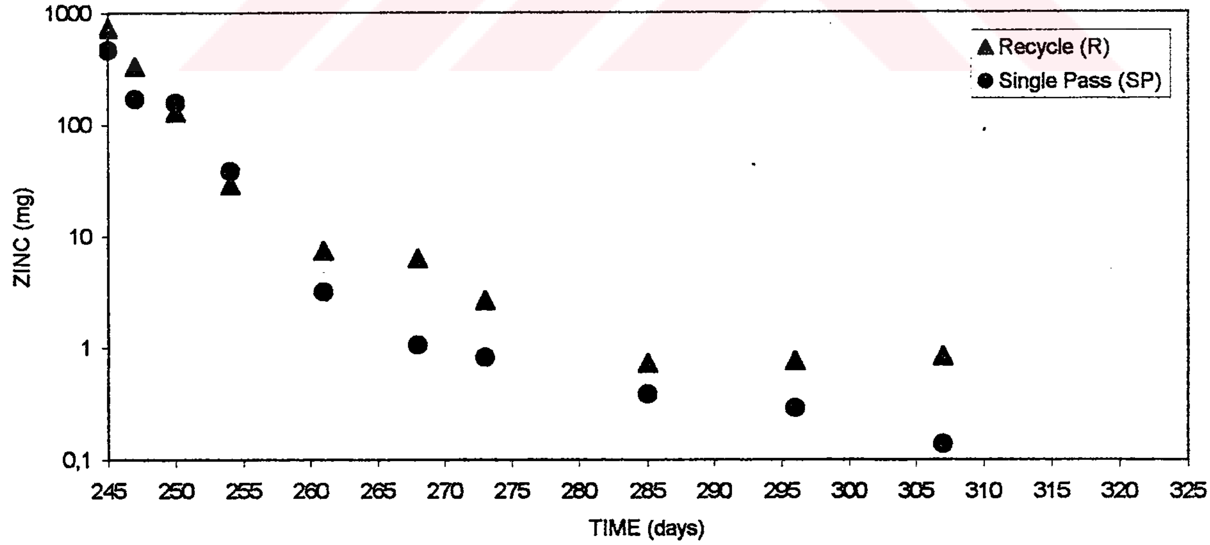
4.32 Leachate Nickel Concentrations from the Recycle and Single Pass Reactors



4.33 Leachate Nickel Masses from the Recycle and Single Pass Reactors



4.34 Leachate Zinc Concentrations from the Recycle and Single Pass Reactors



4.35 Leachate Zinc Masses from the Recycle and Single Pass Reactors

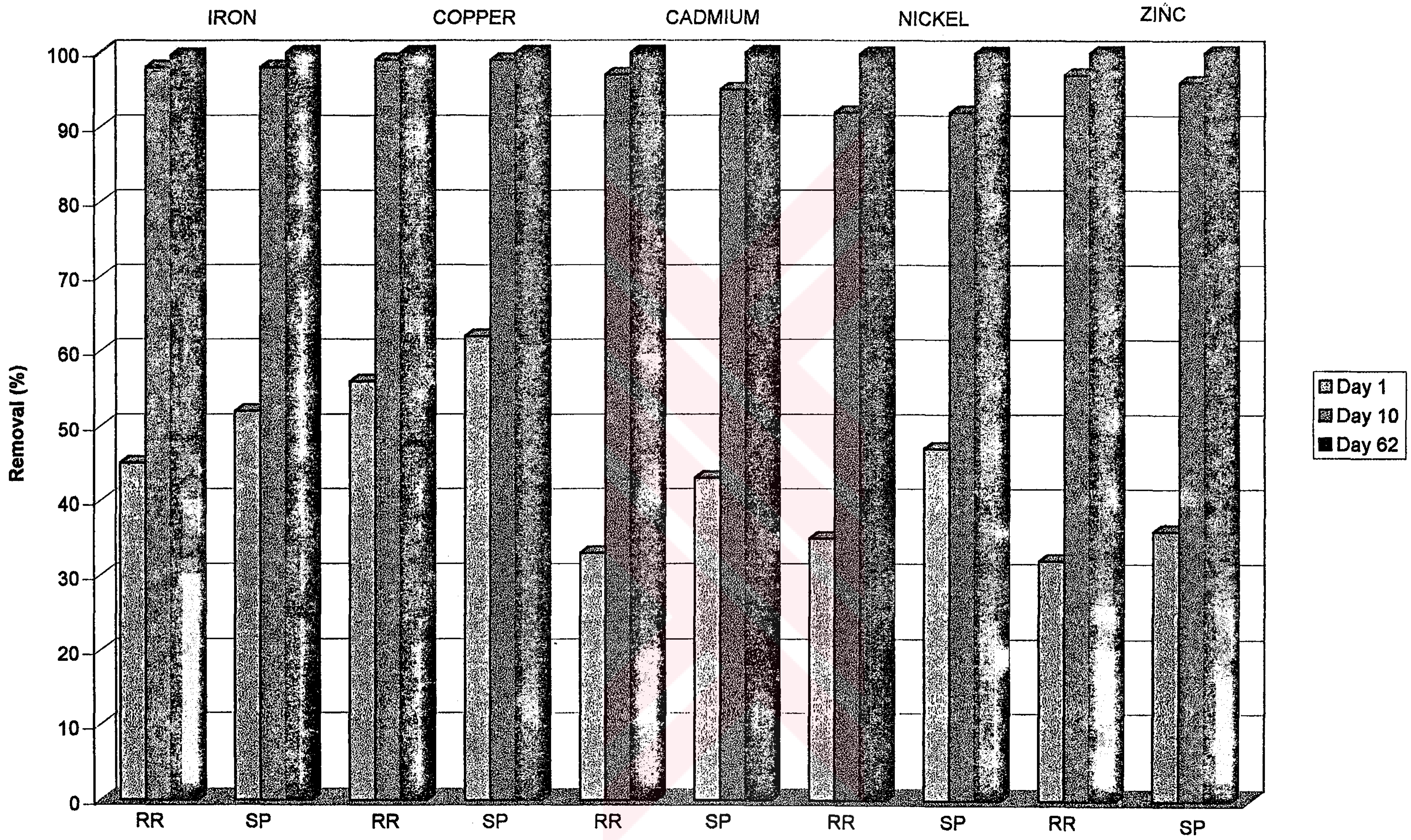
The selected heavy metals were monitored for 62 days. The results of the experiments indicated that firstly, the control of metal solubility was controlled by anions such as sulfate, carbonate and phosphate. Especially Fe^{+3} formed insoluble iron-phosphates together with initial decreased pH values since theoretically , the minimum solubility of $FePO_4$ occurs at pH 5.3 (Metcalf&Eddy, 1991). After the establishment of the reducing environment confirmed by low ORP values, Fe^{+3} and sulfate ions reduced to Fe^{+2} and sulfide respectively. Along with the presence of sulfide, all metals formed in soluble metal-sulfides and the other ions including carbonate, phosphate became free.

As indicated in Figure 4.36 the removal efficiency of the metals was calculated and nearly most of them was removed from the reactors in the first ten days. The removal of heavy metals in recycle reactors was attributed by sulfide precipitation because recirculation enhanced the reduction of sulfate to sulfide. On the other hand, the decline in concentration of heavy metals in single pass reactor was attributed to the effect of washout. Observed higher metal concentrations in the single pass container where leachate was collected from the reactor confirmed these results.

4.2.10. Mass Balance of Heavy Metals and Sulfides

At the end of the study, mass balance computations were performed to better understand the removal efficiency of heavy metals by sulfides. The sulfate salts of selected metals (Fe, Cu, Ni, Cd, Zn) were loaded into the reactors as stoichometrically equivalent quantities given in the Turkish Hazardous Waste Control Regulation and as a manner which does not exceed the toxic sulfide level of 200 mg/L after reduction of sulfate to sulfide and precipitation of sulfide by heavy metals.

Initially loaded heavy metal masses into the recycle and single pass reactors were 2317 mg and 2374 mg for iron, 1094 and 1093 mg for copper, 105 mg and 103 mg for cadmium, 1461 mg and 1490 mg for nickel, 1067 mg and 856 mg for zinc, respectively. On the other hand, initially loaded sulfate masses were 10242 mg in the recycle reactor and 10444 mg in the single pass reactor.

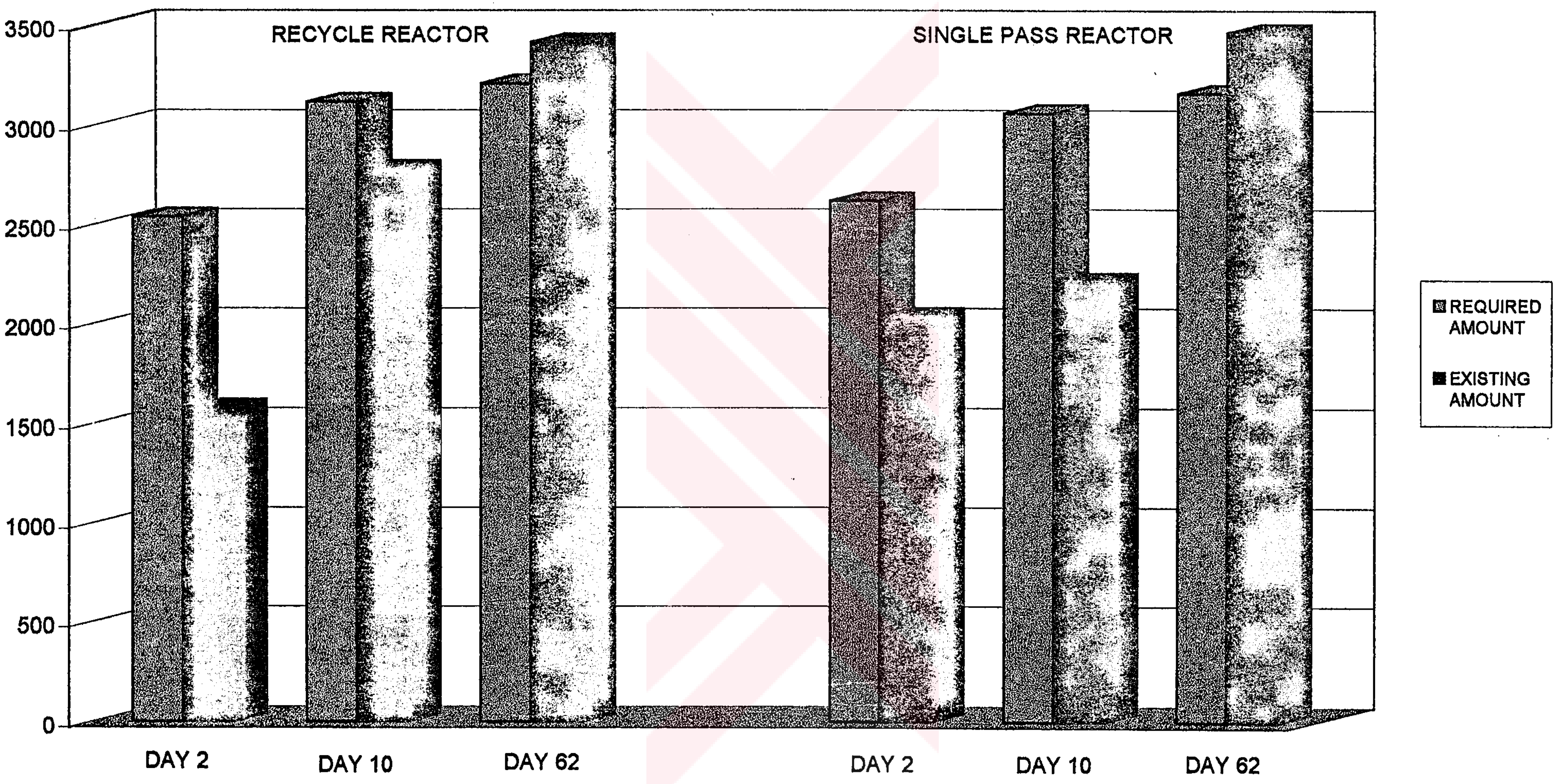


4.36 Removal Efficiency of the Metals for Recycle and Single Pass Reactor

It is rather difficult to make a material balance on heavy metals together with sulfides in landfills due to the presence of many chemical complexes. Metal-sulfide precipitation in both reactors was determined with the following approach; it was assumed that all sulfate concentrations reduced to sulfides and the sulfides formed insoluble metal-sulfides. Along with this approach, theoretical sulfide requirements for metal precipitation and theoretical sulfide in the reactors from sulfate reduction were calculated and presented in Tables of Appendix D and summarized in Figure 4.37.

As indicated in Figure 4.37, the required sulfide amount to immobilize heavy metals was not enough in the first ten days. Therefore, other anions made a contribution to heavy metal precipitation in this time. Towards the end of experiments all sulfates in both reactors were reduced sulfides and along with increased sulfide concentrations, other anions such as CO_3, PO_4 bound with heavy metals were separated and their concentrations increased again in the system. Leachate recirculation also accelerated sulfate reduction and heavy metals formed insoluble metal-sulfide precipitates earlier in the recycle reactor. On the other hand, an increase in CO_3 and PO_4 compounds in the single pass reactor was not observed due to the effect of washout.

After reduction of all sulfate and precipitation of the metals by sulfide compounds, theoretically calculated sulfide amount in systems was found higher measured at the end of the study. This difference between measured sulfide and calculated sulfide comes from escaping H_2S gases which could not monitored during the study, assimilation of sulfide into cell mass and washout mechanism.



4.37 Stoichiometric Amounts for Sulfide (mg)

5. SUMMARY AND CONCLUSIONS

The objective of this research was to better understand the extent of heavy metal attenuation in landfills by means of precipitation as sulfide compounds. The effect of selected heavy metals (Zn, Cu, Cd, Fe, Ni) on solid waste stabilization together with the effect of leachate recirculation on the attenuation mechanisms was also investigated. For this purpose, two landfill simulating bioreactors were used in the laboratory. These reactors were constructed and filled with shredded and compacted municipal solid waste having typical solid waste composition determined for İstanbul region. Two bioreactors one with leachate recirculation, the other without were operated in the constant temperature room of 32 °C to enhance the growth of anaerobic microorganisms. Moreover, moisture addition was done into the bioreactors in order to simulate the annual rainfall. In order to investigate heavy metal attenuation in terms of metal-sulfide precipitation, the reactors were operated under different operational stages for establishment of methanogenic conditions in both reactors before co-disposal since low pH values in landfills having acidogenic phase cause solubilization and mobilization of heavy metals. After ensuring the onset of the methanogenetic conditions in both reactors, the selected heavy metals were added into the simulated landfill reactors to understand landfill assimilative behavior and the effect of leachate recirculation. The metals (Fe, Cu, Ni, Cd, Zn) were prepared by dissolving the metal salts in one liter deionized water and introduced to the reactors according to the amounts suggested for co-disposal under the directives of the Turkish Hazardous Waste Control Regulation.

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

1. To determine the fate of heavy metals and the degree of waste stabilization, the collected gas and leachate samples from both reactors were analyzed on a regular basis for the following parameters: daily gas production and gas composition, COD, pH, alkalinity, phosphate, chloride, ORP, sulfate, sulfide, conductivity and selected heavy metals (Fe, Cu, Ni, Cd, Zn).

The COD values obtained from the recycle reactor have shown an important increase during the first stage as a result of leachate recirculation from the container having high organic content. The addition of 1N KOH buffer did not cause any decrease in COD concentrations due to permanently organic matter addition by recirculation although it increased daily gas production. Leachate recirculation from single pass reactor having low organic content and desirable microbial population provided a decrease in high COD concentrations throughout the second stage. The addition of Na_2CO_3 and the increase in recirculation frequency in the third stage enhanced the conversion of organic matter. In the fourth stage, COD concentrations reached their nearly constant values due to completion of waste stabilization in the reactor. Heavy metal addition did not affect the removal of COD. On the other hand, lower COD values in the single pass reactor continued to decrease as a result of washout and decomposition of the waste. Throughout the second stage of operation, the leachate COD concentrations stayed constant except daily fluctuations by addition of organic carbon from the other reactor. Operation procedure employed during the fourth stage, involving no simulated rainfall water addition, prevented the washout of organic matter. Like waste stabilization in the recycle reactor, single pass reactor was not affected by the addition of heavy metals. As a result, conversion of organic strength in the recycle reactor was enhanced by increase in recirculation frequency and buffer additions. High initial metal concentrations did not cause any toxic effect on microorganisms which provide waste stabilization in both reactor.

While the initial pH values obtained from the recycle reactor reflected acidic values, initial pH in single pass reactor was neutral due to the previous establishment of methanogenic conditions before. An attempt was made to increase the pH of leachate in the recycle reactor by buffering the recycled leachate. This buffer addition provided a slight increase in pH values during the first stage. Along with leachate recirculation from the other reactor, pH values stayed constant in the second stage. Only increase in the frequency of leachate recirculation did not make a contribution to pH values. However, both leachate recirculation and buffer addition increased the pH of system to neutral in a short time. The neutral pH values continued in the same trend until the end of Phase 1 as a result of the establishment of methanogenic population and the completion of conversion of volatile acids. On the other hand, high pH values in the single pass reactor declined slightly due to nearly completed waste stabilization and the washout of alkalinity throughout Phase 1. After the metal addition, a sharp decrease in pH values of the both reactors was observed. This decline was primarily due to the addition of metal solution having acidic properties and precipitation of $CO_3^{=}$ ions contributing to alkalinity with heavy metal addition. After the precipitation of heavy metals by sulfides, the pH values of both reactors returned to their former values. As a consequence, leachate recirculation and buffer additions enhanced the activity of microorganisms and accelerated waste stabilization.

Along with buffer additions in the first stage and the third stage of recycle reactor to enhance waste stabilization, alkalinity concentrations in both reactors throughout Phase 1 remained to be sufficient to buffer the possible effects of the volatile fatty acids released as a result of decomposition of the waste. A decline in the alkalinity concentration in leachate from the single pass reactor was observed due to washout in the system. After metal addition, alkalinity in both reactors reached nearly zero because $CO_3^{=}$ anions providing alkalinity precipitated with heavy metals. While the alkalinity concentration in the recycle reactor reached 1300 mg/L as $CaCO_3$ at the end of experiments, the alkalinity concentration in single pass reached only 700 mg/L as $CaCO_3$ because leachate recirculation enhanced reduction of sulfate to sulfide which is a powerful precipitant for heavy metals and provided to be free of CO_3 ions.

Initial decomposition of high organic materials containing phosphorus caused sharp decrease in the leachate orthophosphate concentrations in the recycle reactor. On the other hand, decrease in orthophosphate concentrations in the single pass reactor was small due to nearly completed waste stabilization. This decrease in single pass reactor was a result of washout mechanism. Along with metal addition, like $CO_3^{=}$ ions, orthophosphates precipitated by metals until the formation of sulfide from sulfate. Greater phosphorus utilization in Phase 1 and earlier release of orthophosphate after sulfide formation during Phase 2 in the recycle reactor have proved once more that the leachate recycle positively effected the enhancement of microbial activity.

Chloride was monitored as a tracer to estimate the effect of dilution. A decrease in chloride concentrations especially in the first stage of the single pass reactor once more proved the existence of washout. After metal addition, increased chloride concentration due to addition of metal salts including chloride began to dramatically decrease in both reactors as a result of washout. This mechanism in the single pass reactor was more effective.

While all ORP values in the single pass reactor were negative due to the existence of highly reducing environment during Phase 1, initial ORP values in the recycle reactor were positive because of the unsuitable sampling procedures and the initial presence of oxygen in the reactor. After the establishment of suitable conditions, ORP values decreased to –200 mV which is a prerequisite for the efficiency of methanogenic activity due to the operational stages employed during Phase 1. The high positive values were monitored together with metal addition due to the presence of oxidized form of metal such as Fe^{+3} and the presence of sulfates in the metal salts. The transition from oxidizing to reducing conditions in the recycle reactor was faster because leachate recirculation accelerated the establishment of reducing environment.

Since highly reducing conditions confirmed by negative ORP values were established in both reactors before, sulfate concentrations were not observed except once or twice during Phase 1. On the other hand, initial high sulfide concentrations decreased to about 5 mg/L in both reactors due to precipitation and washout mechanisms throughout Phase 1. After metal addition, sulfate concentration increased sharply due to usage of metal-sulfate salts and possible sulfides in both reactors precipitated with metals. Along with the onset of reducing conditions, sulfate reduced to sulfide and sulfide began to reappear after the precipitation of all heavy metals. As a conclusion, leachate recirculation accelerated reduction of sulfate and consequently, precipitation of heavy metals with sulfides.

The conductivity of a leachate reflects the total concentration of ionic solutes. After metal addition, high initial conductivity values decreased rapidly due to the washout and the precipitation of sulfides as metal sulfide.

Selected heavy metal concentrations (Fe, Cu, Cd, Ni, Zn) obtained from both reactors have shown the similar decreasing trend during the experimental study as a result of precipitation. Firstly, the control of metal solubility in both reactors was obtained anions as sulfate, carbonate and phosphate due to insufficient initial sulfides. After the establishment of reducing environment confirmed by low ORP values, sulfate reduced to sulfide and all heavy metals precipitated with sulfides while other anions such as phosphate and carbonate became free. About 90% of all heavy metals removed from the reactors within the first 10 days and the potential for the selected heavy metals precipitation with sulfides of the solid waste matrix is $Cu \approx Fe > Cd \approx Zn > Ni$. The removal of heavy metals in the recycle reactor was attributed by sulfide precipitation because recirculation enhanced the reduction of sulfate to sulfide. On the other hand, the decline in heavy metal concentrations in the single pass reactor was attributed to the effect of washout.

2. The unwanted decrease in temperature due to a technical problem from 32°C to 19°C ceased the gas production in the each reactor because the activity of microorganisms are severely affected.

3. Leachate recirculation served to facilitate degradation, conversion and immobilization of refuse constituents. The environment in the recycle reactor was more suitable for the rapid development of the desired microorganisms and for sulfate reduction along with the enhanced precipitation of heavy metals due to increased contact of leachate with the solid matrix. On the other hand, leachate from the single pass reactor was constantly washout from the system, taking away nutrients, substrates and heavy metals.

4. The frequency of leachate recirculation has proved to be an important factor for high degree of organic release and their removal. Recirculation frequency was gradually increased to three times per week. Although every attempt to increase frequency of recirculation was followed by positive changes in the monitored parameters, the best results were obtained together with the buffer addition.

5. Leachate recirculation from single pass container having low organic content and higher buffer capacity and desired acclimated anaerobic microorganisms to the recycle reactor enhanced waste stabilization during the second stage. On the other hand, substrate deficiency of microorganism in the single pass reactor was prevented by the addition of leachate from the recycle reactor having high organic carbon sources.

6. Leachate buffering together with recirculation enhanced the establishment of desired methanogenic population responsible for conversion of organics to methane and carbon dioxide. Combination of leachate buffering with three times recirculation per week provided high degree of waste stabilization as reflected by gas and leachate indicator parameters.

7. Heavy metal inhibition is considered the most important factor causing delays in the release and conversion of organic pollutants in landfills. Analysis of the data indicated that after metal addition into both reactors, organic fraction of waste continued to decrease since metal salts were loaded to the reactors according to the amounts suggested for codisposal under the directives of the Turkish Hazardous Waste Control Regulation to prevent inhibition of microbially mediated processes during waste stabilization.

8. When sulfide concentration was very low or insufficient, the removal of the metals was controlled by other anions such as phosphates and carbonates until the reduction of sulfate coming from loaded metals salts into the reactors. Along with the increase in sulfide concentration, anions became free and the selected heavy metals (Fe, Cu, Cd, Ni, Zn) precipitated with sulfides within 10 days. The removal efficiency of selected metals in the solid waste matrix is Cu $\approx$ Fe> Cd $\approx$ Zn > Ni. The removal of heavy metals in the recycle reactor was enhanced by recirculation. On the other hand , the decline in concentration of heavy metal concentrations in the single pass reactor was attributed to the effect of washout.

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

1. The leachate recirculation management strategy offers opportunities for more rapid waste stabilization, including attenuation of codisposed heavy metals.

2. Utilization of buffer solutions of KOH and Na_2CO_3 together with leachate recirculation further enhanced the waste stabilization and prevented possible acid inhibition.

3. The exchange of leachate between reactors provided desirable microbial population to initiate accelerated waste stabilization in the recycle reactor and required organic carbon sources for methanogens in the single pass reactor to prevent substrate deficiency.

4. Methanogenic populations within both reactors were essentially unaffected by application of heavy metal loading which were in accordance with the Turkish Hazardous Waste Regulation.

5. The selected heavy metals were removed by sulfide precipitation and the removal efficiency was as follows; $Cu \approx Fe > Cd \approx Zn > Ni$.

6. RECOMMENDATIONS

In this study, the selected heavy metal (Fe, Cu, Zn, Cd, Ni) was monitored as total and sulfide was measured in leachate. For further studies, it was recommended that the measurement of all sulfides such as in gas phase, in solid waste for the establishment of detailed mass balance and the measurement of soluble heavy metals.

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APPENDIX A

TABLE A-1 Operational Stages Emloyed Throughout the Experimental Study

WEEKS	DAYS	SINGLE PASS REACTOR			RECYCLE REACTOR		
		LEACHATE (mL)	WATER (mL)	CHEMICAL	LEACHATE (mL)	WATER (mL)	CHEMICAL
1	1				1000		
	3		500			500	
	7				1000		
2	12		500			500	
	14				1000		
3	19		500			500	
	21				1000		
4	26		500			500	
	28				1000		
5	33		500			500	
	35				1000		
6	40		500			500	
	42				1000		
7	47		500			500	
	49				1000		
8	54		500			500	
	56				1000		200 mL KOH
9	61		500			500	
	63				1000		200 mL KOH
10	68		500			500	
	70				1000		200 mL KOH
11	75		500			500	
	77				1000		200 mL KOH
12	82		500			500	
	84				1000		170 mL KOH

WEEKS	DAYS	SINGLE PASS REACTOR			RECYCLE REACTOR		
		LEACHATE (mL)	WATER (mL)	CHEMICAL	LEACHATE (mL)	WATER (mL)	CHEMICAL
13	89		500			500	
	91				1000		
14	96		500			500	
	98				1000		
15	103				1000		from SP to RR
	105		500		1000	500	
16	110				1000		from SP to RR
	112				1000	500	
	114		500	600 mg/L COD			
17	117				1000		from SP to RR
	119				1000	500	
18	123		250	800 mg/L COD			
	124				1000		from SP to RR
	126		250	800 mg/L COD	1000	500	
19	131				1000		from SP to RR
	133				1000	500	
	135		500	1000 mg/L COD			
20	138				1000		
	140				1000	500	
	142		500	2000 mg/L COD	1000		100 g/L Na2CO3
21	145				1000		100 g/L Na2CO3
	147				1000	500	100 g/L Na2CO3
	149				1000		100 g/L Na2CO3
22	153				1000		100 g/L Na2CO3
	154		500	2500 mg/L COD (114 mL)	1000	500	100 g/L Na2CO3
	156				1000		100 g/L Na2CO3

WEEKS	DAYS	SINGLE PASS REACTOR			RECYCLE REACTOR		
		LEACHATE (mL)	WATER (mL)	CHEMICAL	LEACHATE (mL)	WATER (mL)	CHEMICAL
23	159				1000		
	160	200	500	8885 mg/LCOD			
	161				1000	500	
	163				1000		
24	166				1000		
	167	500		6238 mg/LCOD			
	168		500				
	170				1000	500	
25	173				1000		
	177	500	500	5707 mg/LCOD		500	
26	182	500		5555 mg/LCOD	1000		
	184		500			500	
27	188	500		3577 mg/LCOD	1000		
	191		500			500	
28	195	500		2217 mg/LCOD	1000		
	198		500			500	
29	203	500		770 mg/LCOD[1]	1000		
	205		500			500	
30	210				1000		
	212					500	
31	218				1000	500	
32	225				1000	500	
33	233				1000	500	
34	239				1000	500	
35	245		1000	1 L metal solution	1000		1 L metal solution
	247		500			500	

WEEKS	DAYS	SINGLE PASS REACTOR			RECYCLE REACTOR		
		LEACHATE (mL)	WATER (mL)	CHEMICAL	LEACHATE (mL)	WATER (mL)	CHEMICAL
36	252				1000		
	254		500			500	
37	259				1000		
	261		500			500	
38	268		500		1000	500	
39	273				1000		
	275		500			500	
40	282		500		1000	500	
41	289		500		1000	500	
42	296		500		1000	500	
44	307		500		1000	500	

[1] this recyle was made from the single pass reactor while the others was made from the recycle reactor

APPENDIX B

TABLE B-1 LEACHATE CHARACTERISTICS IN RECYCLE REACTOR

DATE	DAYS	PH	ORP mV	COD mg/L	PO4 mg/L	SO4 mg/L	Alkalinity mg/L	Cl mg/L	S mg/L	Conductivity mS/cm
02.02.00	0	5,61		10020						
03.02.00	1	5,60								
04.02.00	2	5,60		11169	171	0	2493	410	40	
07.02.00	5	5,67		11497						
08.02.00	6	5,63		11826	189	0	2493	223		
10.02.00	8	5,78		17241						
11.02.00	9	5,83	-137						34	
14.02.00	12	5,60		15600						
15.02.00	13	5,86	29,5	15600						
16.02.00	14	5,76	27,5	16913						
17.02.00	15	5,77	19,3	17569	217	15	2592	280	33	
18.02.00	16	5,76		17608						
21.02.00	19	5,82	3,5	17871						
22.02.00	20	5,55	13	17713						
23.02.00	21	5,54	12,9	17976						
24.02.00	22	5,52	11,5	17608			2094	260		
25.02.00	23			19184	218	75				
28.02.00	26	5,42								
29.02.00	27	5,52	40	18133						
01.03.00	28	5,50	3	18921						
02.03.00	29	5,51		18921	217	135	1945	299	24	
03.03.00	30	5,51	2,3	18921						
06.03.00	33	5,48	-42	17083						
07.03.00	34	5,49	-22	17608						
08.03.00	35	5,51	-60,3							
09.03.00	36	5,49	-75		226	185				

DATE	DAYS	PH	ORP mV	COD mg/L	PO4 mg/L	SO4 mg/L	Alkalinity mg/L	Cl mg/L	S mg/L	Conductivity mS/cm
10.03.00	37	5,52	-49	17870						
11.03.00	38	5,50	-45				2094		37,6	
13.03.00	40							296		
14.03.00	41	5,61	0	19708						
15.03.00	42	5,47	-4	16558	216,6					
18.03.00	45	5,52	-21,5	18396				301		
20.03.00	47	5,50	-30,3							
21.03.00	48	5,51	-38	19205						
22.03.00	49	5,56	-73,5							
23.03.00	50	5,60	-59	18106	191,2	140	2293		21,2	
24.03.00	51	5,58	-85							
27.03.00	54	5,76	-122	17006						
28.03.00	55	5,59	-114							
29.03.00	56	5,62	-101,5	18106						
30.03.00	57	5,89	-106,3	18106	151,5	90	2392	328	31,2	
31.03.00	58	5,82	-116							
03.04.00	61	5,82	-129							
04.04.00	62	5,76	-116	19205						
05.04.00	63	5,70	-88	17556						
06.04.00	64	5,88	-85	17556	145,8	10	2000	242	32	
10.04.00	68	5,85	-96,7	17556						
11.04.00	69	5,90	-80							
12.04.00	70	5,92	-85	20306						
13.04.00	71	5,85	-82,7	19755						
14.04.00	72	5,86	-74,3	18381	158,3	35	3000	378	33,6	
17.04.00	75	5,81	-63	19205						
18.04.00	76	5,81	-37	19755						

DATE	DAYS	PH	ORP mV	COD mg/L	PO4 mg/L	SO4 mg/L	Alkalinity mg/L	Cl mg/L	S mg/L	Conductivity mS/cm
19.04.00	77	5,80	-77,3	19755	174,1	5	3112	384	32,4	
20.04.00	78	6,03	-76	19205						
21.04.00	79	6,03	-80,3	20855						
24.04.00	82	6,01	-74,3	20855						
25.04.00	83	5,98	-95,7	20305						
26.04.00	84	5,93	-104	18666	135	0	3112	233	33,2	
27.04.00	85	6,03	-65,5	20306						
28.04.00	86	6,04	-81	19480						
01.05.00	89	5,95	-112,7							
02.05.00	90	5,96	-136,3							
03.05.00	91	5,95	-99,5	19205	131,7	0	3005	194	24,4	
04.05.00	92	5,84	-115,3							
05.05.00	93	5,82	-115,3							
08.05.00	96	5,91	-119,7							
09.05.00	97	5,88	-130,5							
10.05.00	98	5,90	-118,3							
11.05.00	99	5,76	-113,5		150,4	0	3219	379	32	
15.05.00	103	5,81	-141,3							
18.05.00	106	5,99	-154	19206	99	2	2790	253		
19.05.00	107	5,83	-174	17830						
22.05.00	110	5,97	-156	17666					24,4	
23.05.00	111	6,02	-160	16456						
24.05.00	112	6,14	-152	17940	134	16	2683	223		
26.05.00	114	6,00	-61							
29.05.00	117	5,91	-172	164556						
30.05.00	118	6,15	-156	15851						
01.06.00	120	6,27	-191	15906						

DATE	DAYS	PH	ORP mV	COD mg/L	PO4 mg/L	SO4 mg/L	Alkalinity mg/L	Cl mg/L	S mg/L	Conductivity mS/cm
05.06.00	124	6,07	-164	16456	108	4	2951	262	8,4	
06.06.00	125	6,18	-156	17280						
07.06.00	126	6,04	-151	15906						
08.06.00	127		-76							
12.06.00	131	6,09	-119	11480						
13.06.00	132	6,05	-117	11109						
14.06.00	133	6,18	-117	11109						
15.06.00	134	5,83	-66	11604			3081			
16.06.00	135	5,79	-76	12840						
19.06.00	138	5,87		11109	92	62	2424	267	1,2	
20.06.00	139	5,81		11109						
21.06.00	140	5,86		13583						
22.06.00	141	5,79		11604						
23.06.00	142	5,80		12593						
26.06.00	145	5,98		12098	80,2		2020	272	7,2	
27.06.00	146	6,02		10615		2				
28.06.00	147	5,94		10615						
29.06.00	148	5,93		11100						
30.06.00	149	5,89		12099						
03.07.00	152	6,05		12099						
04.07.00	153	6,26		10615						
05.07.00	154	6,62		11110						
06.07.00	155	6,46		9380	53	14	2525	253	3,2	
07.07.00	156	6,33		9379						
10.07.00	159	6,98		8885						
12.07.00	161	6,80		7154	50,1	0	3030	204	7,2	
14.07.00	163	7,02		7896						

DATE	DAYS	PH	ORP mV	COD mg/L	PO4 mg/L	SO4 mg/L	Alkalinity mg/L	Cl mg/L	S mg/L	Conductivity mS/cm
17.07.00	166	7,04		7154						
18.07.00	167	6,81		6238						
19.07.00	168	6,88		5431						
20.07.00	169	6,91								
21.07.00	170	6,89		5060	25	0	2946	233		
24.07.00	173	7,05		4500					2,8	
25.07.00	174	7,18		5090						
26.07.00	175	7,47		5707						
31.07.00	180	6,62		5308						
01.08.00	181	6,48		5555						
03.08.00	183	6,75		4071						5,50
04.08.00	184	6,85		3948	22,4	0	2828	185	5,6	
08.08.00	188	6,93		3577						
09.08.00	189	6,71	-158	4442						
10.08.00	190	6,81	-181	4220	27	0	2626	165	5,6	
11.08.00	191	6,85	-165	4442						
14.08.00	194		-180							
15.08.00	195	7,10		2217						
16.08.00	196	6,85	-145	2617						
17.08.00	197	6,86	-158	2617	23,2	0	2813	155	5,6	
18.08.00	198	6,97	-188	1912						
22.08.00	202	7,10	-210	1294						
24.08.00	204	7,18	-205	2036	28,7	0	2588	97	5,4	
25.08.00	205	6,92	-210							
28.08.00	208	6,95		1356						
30.08.00	210	6,96	-158	1541						
31.08.00	211		-261	1420			2475	112		

DATE	DAYS	PH	ORP mV	COD mg/L	PO4 mg/L	SO4 mg/L	Alkalinity mg/L	Cl mg/L	S mg/L	Conductivity mS/cm
01.09.00	212	7,09		1265	25,9	0				
05.09.00	216	6,88	-214	1294						
07.09.00	218	7,17		1141	29,2	0	2813	145		
08.09.00	219	7,04								
11.09.00	222	6,88	-116							
12.09.00	223		-126						0	
14.09.00	225	7,05	-240		24,9	0	2250	146		
19.09.00	230	6,97								
20.09.00	231		-177	1657					2,8	
22.09.00	233			1448						
25.09.00	236	6,99	-175	1175	25,2	0	2250	87		3,37
26.09.00	237	7,09		1309						
28.09.00	239		-102	1065						
29.09.00	240	6,90	-153							
02.10.00	243	7,14			22,3	8		87		
03.10.00	244	6,92	-91	1309		2	1631		3,4	
04.10.00	245	6,99								
05.10.00	246	4,43	177							11,68
06.10.00	247	4,87	140	752	6,3	5800	113	971	1,6	7,81
09.10.00	250	5,14	205	809						6,32
11.10.00	252	5,55	155	968	1,2	3600		612	0,8	5,80
13.10.00	254	5,74		1309						4,05
16.10.00	257	6,17		1274			844	388		4,33
18.10.00	259	6,32	40	1226	2,5	1900			0,8	4,13
20.10.00	261	6,59	5	1274						4,06
23.10.00	264	6,58	140	891						3,55
25.10.00	266	6,54	-160		2,5	500			6	3,49

DATE	DAYS	PH	ORP mV	COD mg/L	PO4 mg/L	SO4 mg/L	Alkalinity mg/L	Cl mg/L	S mg/L	Conductivity mS/cm
27.10.00	268	6,69	-30	1200						3,68
30.10.00	271	6,67	-72	1100			1344			3,47
31.10.00	272	6,65	-43		3,1	320		328	4,8	3,26
03.11.00	275	6,61								3,61
06.11.00	278	6,69		600			1152			3,11
10.11.00	282	6,90	-357	961	7,54	200	1632	299	2,4	3,08
13.11.00	285	6,78	-304			105				3,10
17.11.00	289	6,91	-308	682				241	2,4	3,02
24.11.00	296	6,81	-301	724		0		260	2,4	2,93
29.11.00	301				18,32	0				
05.12.00	307	6,93	-304	430	19,35	0	1300	194	2,4	2,87

TABLE B-2 LEACHATE CHARACTERISTICS IN SINGLE PASS REACTOR

DATE	DAYS	PH	ORP mV	COD mg/L	PO4 mg/L	SO4 mg/L	Alkalinity mg/L	Cl mg/L	S mg/L	Conductivity mS/cm
02.02.00	0	7,78		1159						
03.02.00	1	7,75								
04.02.00	2	7,82		1815						
07.02.00	5	8,04								
08.02.00	6	7,23		1583	56	0	4038	371	12	
10.02.00	8		-174	1020						
11.02.00	9	7,50	-210	1382						
14.02.00	12	7,55	-92	936						
15.02.00	13	7,58	-192	1054						
16.02.00	14	7,43	-95	1120						
17.02.00	15	7,96	-110	976						
18.02.00	16	7,45			59	0	4187	304		
21.02.00	19	7,41	-182	1776						
22.02.00	20	7,25	-112	1474						
23.02.00	21	7,22	-114	1540						
24.02.00	22	7,16	-90	1382			3888	304		
25.02.00	23	7,47		1409	56	0				
28.02.00	26	7,62		1146						
29.02.00	27	7,14	-176	1645						
01.03.00	28	7,16	-163	1383						
02.03.00	29	7,16	-184	1146	55	10	3640	222	31	
03.03.00	30			1382						
06.03.00	33	7,38	-175	1054						
07.03.00	34	7,15	-220	989						
08.03.00	35	7,18	-170							
09.03.00	36	7,19	-246	1054	50	0				

DATE	DAYS	PH	ORP mV	COD mg/L	PO4 mg/L	SO4 mg/L	Alkalinity mg/L	Cl mg/L	S mg/L	Conductivity mS/cm
10.03.00	37	7,16	-193	1054						
11.03.00	38	7,17	-201				3390		23,2	
13.03.00	40	7,22	-167	1120				242		
14.03.00	41	7,19	-163	1513						
15.03.00	42	7,16	-166	1250	45,8					
18.03.00	45	7,26	-175				2991	214		
20.03.00	47	7,30	-166							
21.03.00	48	7,12	-235	2194						
22.03.00	49	7,21	-197							
23.03.00	50	7,15	-270	1026	46,8	10	2991	165	19,6	
24.03.00	51	7,16	-210							
27.03.00	54	7,37	-235	1127						
28.03.00	55	7,06	-235							
29.03.00	56	7,09	-174	1365						
30.03.00	57	7,04	-196	820	49,5	10	2692	154	16	
31.03.00	58	7,11	-166							
04.04.00	62	7,10	-168	888						
05.04.00	63	7,11	-182	820						
06.04.00	64	7,06	-186	751	42,2	10	2500	126	18	
10.04.00	68	7,10	-182	922						
11.04.00	69	7,00	-188							
12.04.00	70	7,01	-164	1026						
13.04.00	71	7,01	-163	916						
14.04.00	72	6,95	-167	854	42,8	40	2550	170	13,6	
17.04.00	75	7,05	-173	820						
18.04.00	76	7,01	-172	806						
19.04.00	77	7,04	-164	854	40,8	10	2468	121	12	

DATE	DAYS	PH	ORP mV	COD mg/L	PO4 mg/L	SO4 mg/L	Alkalinity mg/L	Cl mg/L	S mg/L	Conductivity mS/cm
20.04.00	78	7,03	-173	751						
21.04.00	79	6,99	-164	751						
24.04.00	82	7,00	-112	888						
25.04.00	83	7,03	-197	717						
26.04.00	84	7,06	-211	737						
27.04.00	85	6,96	-176	855	43,2	20	2361	126	14,8	
28.04.00	86	6,93	-159	751						
01.05.00	89	6,85	-256							
02.05.00	90	6,78	-254							
03.05.00	91	6,79	-230	613	36,85	0	2146	126	6,4	
04.05.00	92	6,88	-172							
05.05.00	93	6,88	-177							
08.05.00	96	6,93	-193							
09.05.00	97	6,99	-209							
10.05.00	98	6,99	-206							
11.05.00	99	6,88	-204		40,15	0	2253	107	10,8	
15.05.00	103	6,98	-241	750						
16.05.00	104	6,95	-236	648						
18.05.00	106	6,97	-243	682	45,5	0	2361	126		
19.05.00	107	6,97	-250	650						
22.05.00	110	6,85	-243	614					4,2	
23.05.00	111	6,80	-262	641						
24.05.00	112	6,79	-243	682	38,85	0				
25.05.00	113						1932	106		
26.05.00	114	6,75	-245							
29.05.00	117	6,79	-278	511						
30.05.00	118	6,85	-251	483						

DATE	DAYS	PH	ORP mV	COD mg/L	PO4 mg/L	SO4 mg/L	Alkalinity mg/L	Cl mg/L	S mg/L	Conductivity mS/cm
01.06.00	120	6,90	-238	545						
05.06.00	124	6,90	-243	503	40	0	1878	146	3,2	
06.06.00	125	6,94	-215	455						
07.06.00	126	6,97	-162	480						
08.06.00	127	6,80								
12.06.00	131		-90	859						
13.06.00	132	6,99	-164	729						
14.06.00	133	6,87	-167	407			1919			
16.06.00	135	6,81	-70	438						
19.06.00	138	6,86		359	34	150	1667	131	3,2	
20.06.00	139	6,77								
21.06.00	140	6,80		300						
22.06.00	141	6,83		314						
23.06.00	142	6,87		302						
26.06.00	145	6,78		481	30,8			58	4	
27.06.00	146	6,80		308		10				
28.06.00	147	6,84		432						
29.06.00	148	6,86		333						
30.06.00	149	6,84		358						
03.07.00	152	6,87		420						
04.07.00	153	6,87		457						
05.07.00	154	6,88		357						
06.07.00	155	7,04		654	29,2	5	1717	49	1,6	
07.07.00	156	6,86		308						
10.07.00	159	6,79		340						
12.07.00	161	6,78		956	24,5	2	1414	272	4,8	
14.07.00	163	6,80		407						

DATE	DAYS	PH	ORP mV	COD mg/L	PO4 mg/L	SO4 mg/L	Alkalinity mg/L	Cl mg/L	S mg/L	Conductivity mS/cm
17.07.00	166	6,84		394						
19.07.00	168	7,08		1998						
20.07.00	169	6,95								
21.07.00	170	6,96		676	22,35	2	2134	78		
24.07.00	173	7,09		333					3,2	
25.07.00	174	6,90		271						
26.07.00	175	6,93		407						
31.07.00	180	7,02		444						
01.08.00	181	6,90		432						
03.08.00	183	7,00		593						4,64
04.08.00	184	7,08		494	30	0	2323	107	4	
08.08.00	188	7,05		901						
09.08.00	189	7,01	-146	877						
10.08.00	190	6,84	-219	506	31,4	0	2323	87	4,4	
11.08.00	191	6,97	-246	432						
15.08.00	195			531						
16.08.00	196	6,95	-207	1544						
17.08.00	197	6,95	-224	556	30,1	0	2588	87	4	
18.08.00	198	7,01	-195	580						
22.08.00	202	7,01	-219	308						
23.08.00	203			370						
24.08.00	204		-238	333	29,2	750	1913	78	5	
25.08.00	205	6,91	-250							
28.08.00	208	6,94		358						
30.08.00	210	6,91	-240	284						
31.08.00	211		-305	327				49		
01.09.00	212	7,05	-280	333	28,1	460	1688		6	

DATE	DAYS	PH	ORP mV	COD mg/L	PO4 mg/L	SO4 mg/L	Alkalinity mg/L	Cl mg/L	S mg/L	Conductivity mS/cm
05.09.00	216	6,89	-253	302						
07.09.00	218	7,17		333	3,2	450	1856	49		
08.09.00	219	7,08								
11.09.00	222	6,98								
12.09.00	223		-224						5,6	
14.09.00	225	7,15	-302		32,5	125	2250	107		
19.09.00	230	7,35	-268	394						
20.09.00	231			394					5,6	
22.09.00	233			394						
25.09.00	236	7,32		380	37,2	0	2363	48,6		4,14
26.09.00	237	7,44	-232	394						
28.09.00	239			290						
29.09.00	240	7,04								
02.10.00	243				37	0		68		
03.10.00	244	7,33	-120				2531			
04.10.00	245	7,14	-152						3,6	
05.10.00	246	4,98								10,85
06.10.00	247	5,05	123	262	1,4	6200	169	923	2,4	9,00
09.10.00	250	5,19	95	220						6,80
11.10.00	252	5,88	89	227	0,6	4000			0	6,30
13.10.00	254	5,87		234			113	855		7,24
16.10.00	257	6,12		200			394			4,71
18.10.00	259	6,32	30	248	3	2700		447	0	4,83
20.10.00	261	6,45	80	227						4,74
23.10.00	264	6,25	3	200						
25.10.00	266	6,37	-133		1,05	1800		366	0	3,80
27.10.00	268	6,60	88	185						3,74

DATE	DAYS	PH	ORP mV	COD mg/L	PO4 mg/L	SO4 mg/L	Alkalinity mg/L	Cl mg/L	S mg/L	Conductivity mS/cm
30.10.00	271	6,35	0				576			2,52
31.10.00	272	6,39	0		0,5	860		337	0	2,98
03.11.00	275	6,36								3,11
06.11.00	278	6,40		192			672			2,55
10.11.00	282	6,70	-132	138	0,88	740	480	347	0	2,80
13.11.00	285	6,54	-78							2,25
17.11.00	289	6,68	-120	138				279	0,8	2,41
24.11.00	296	6,74	-180	138				173	0,4	2,11
29.11.00	301				1,76					
05.12.00	307	6,98	-150	138	2,32	125	700	116	1,6	2,06

TABLE B-3 CUMULATIVE GAS PRODUCTION IN BOTH REACTOR (mL)

Days	Recycle R	Single Pass
0	500	2000
1	500	4000
2	995	5700
3	995	5700
4	995	5700
5	995	5700
6	1495	8200
7	1765	10400
8	2125	12400
9	2585	14500
10	2895	16120
11	3245	18320
12	3625	20320
13	4295	22820
14	4565	24320
15	5185	26820
16	5425	29120
17	5425	29120
18	5425	29120
19	5425	29120
20	5575	31620
21	5735	33820
22	5875	35820
23	6275	37720
24	6275	37720
25	6275	37720
26	6525	40220
27	6875	42420
28	6975	44720
29	7135	46720
30	7295	48820
31	7295	48820
32	7295	48820
33	7295	48820
34	7545	51020
35	7580	53220
36	7580	53220
37	7580	53220
38	7995	55720
39	7995	55720
40	8245	57620
41	8495	59870
42	8695	61970
43	8895	64070
44	9095	66070
45	9295	68070
46	9555	70170
47	9815	72070
48	10075	74170
49	10175	76170
50	10275	78270
51	10375	80270
52	10375	80270
53	10375	80270
54	10375	80270
55	10475	82370
56	10675	84370
57	10875	86370
58	11075	88320
59	11475	88320

Days	Recycle R	Single Pass
60	11875	88320
61	12325	90320
62	12775	92270
63	13105	94270
64	13435	96170
65	13765	98120
66	13765	98120
67	13765	98120
68	14765	100120
69	15765	102120
70	16715	104020
71	16715	105020
72	16715	106520
73	16715	107320
74	17615	109220
75	18415	111120
76	19215	113020
77	19215	114820
78	19215	115820
79	19215	115820
80	19215	115820
81	19215	115820
82	19215	115820
83	19215	116220
84	19215	116220
85	19215	116220
86	19215	116220
87	19215	116220
88	19215	116220
89	19215	116220
90	19215	116220
91	19215	116220
92	19215	116220
93	20215	118220
94	20515	118220
95	20815	118220
96	21115	118220
97	21415	119040
98	21840	121040
99	22265	122840
100	22515	123640
101	22765	123640
102	23015	123640
103	23265	125640
104	24065	126640
105	24915	127640
106	24915	127640
107	24915	127640
108	24915	127640
109	24915	127640
110	25715	129040
111	26715	129590
112	27615	130140
113	28565	130640
114	29565	130640
115	29565	130640
116	29565	130640
117	30565	132090
118	31565	133590
119	32565	135090

Days	Recycle R	Single Pass
120	33565	136490
121	34565	137990
122	34565	137990
123	34565	137990
124	35565	139490
125	36565	140890
126	37365	142490
127	38265	143990
128	38265	143990
129	38265	143990
130	38265	143990
131	38265	145190
132	39065	145490
133	39065	147190
134	40065	148890
135	40865	150590
136	40865	150590
137	40865	150590
138	40865	150590
139	41665	151440
140	41665	152290
141	42565	152990
142	42565	153690
143	42565	153690
144	42565	153690
145	43315	154115
146	44065	154540
147	45065	154965
148	45565	155390
149	46065	156390

Days	Recycle R	Single Pass
150	46065	156390
151	46065	156390
152	47065	157290
153	48065	158190
154	49065	158190
155	51065	158190
156	53065	159090
157	53065	159090
158	53065	159090
159	55065	159290
160	57065	159490
161	59065	159690
162	61065	159890
163	63065	160090
164	63065	160090
165	63065	160090
166	65065	160590
167	67065	161090
168	71065	161590
169	73065	162090
170	75065	162590
171	75065	162590
172	75065	162590
173	77065	163590
174	80765	164590
175	84765	165090
176	88765	165590
177	92365	165590
178	92365	165590
179	92365	165590

Days	Recycle R	Single Pass
180	95365	165870
181	98765	166150
182	102765	166430
183	106565	166710
184	110565	166830
185	110565	166950
186	110565	167070
187	114165	167190
188	117565	167310
189	121565	167810
190	125165	168310
191	129365	168560
192	129365	168810
193	129365	169060
194	132365	169310
195	135965	169910
196	139965	170310
197	144065	170710
198	148065	170960
199	148065	171210
200	148065	171460
201	152065	171710
202	155665	171838
203	159865	171966
204	163765	172094
205	166765	172222
206	166765	172350
207	166765	172478
208	170765	172606
209	174665	172822
210	178865	173038
211	183365	173254
212	187365	173479
213	187365	173704
214	187365	173929
215	190965	174154
216	194965	174334
217	199165	174534
218	203165	174734
219	203165	174934
220	203165	175134
221	203165	175334
222	207665	175514
223	212165	175694
224	215765	175874
225	219865	176054
226	223765	176234
227	223765	176234
228	223765	176234
229	227865	176414
230	231965	176594
231	235565	176774
232	239765	176954
233	243765	177134
234	243765	177134
235	243765	177134
236	247765	177204
237	252265	177274
238	255265	177344
239	259465	177414

Days	Recycle R	Single Pass
240	262965	177484
241	262965	177484
242	265465	177554
243	268465	177624
244	274065	178624
245	278065	178694
246	281665	178757
247	285265	178820
248	285265	178883
249	285265	178946
250	289765	179009
251	289765	179072
252	292265	179135
253	292265	179198
254	295765	179261
255	295765	179324
256	295765	179387
257	298765	179450
258	298765	179513
259	302265	179576
260	302265	179639
261	302265	179702
262	306265	179702
263	306265	179702
264	308765	179762
265	308765	179822
266	312765	179882
267	312765	179942
268	316265	180002
269	316265	180062

Days	Recycle R	Single Pass
270	316265	180122
271	320265	180182
272	320265	180242
273	324765	180302
274	324765	180402
275	328265	180502
276	328265	180602
277	328265	180702
278	332265	180802
279	332265	180902
280	335765	181002
281	335765	181102
282	338765	181202
283	338765	181273
284	338765	181344
285	341265	181415
286	341265	181486
287	341265	181557
288	341265	181628
289	343765	181699
290	343765	181770
291	343765	181841
292	343765	181912
293	343765	181983
294	343765	182054
295	343765	182125
296	346765	182196
297	346765	182286
298	346765	182376
299	346765	182466

Days	Recycle R	Single Pass
300	346765	182556
301	350265	182646
302	350265	182736
303	350265	182826
304	350265	182916
304	350265	183006
306	350265	183096
307	353765	183186

TABLE B-4 GAS COMPOSITION IN BOTH REACTORS (%)

	Recycle Reactor			Single Pass Reactor		
DAYS	AIR	CH_4	CO_2	AIR	CH_4	CO_2
51	75.80	12,32	11,88			
72	89.22	10,1	0,68			
79	73.72	15,93	10,35	13,85	72,74	13,41
86	89.01	7,92	3,07	24,6	61,67	13,73
93	72.40	16,08	11,52			
107	65.57	19,97	14,46	24,43	65,23	10,34
129	74.12	14,94	10,94	16,27	71,35	12,38
141	60.12	24,72	15,16	11,96	74,38	13,66
148	51.36	31,74	16,9	30,97	58,14	10,89
183	31.63	31,34	37,03			
197	36.32	27,77	35,91			
212	36.29	28,76	34,95	16,56	43,13	40,31
219	44.56	33,17	22,27	26,59	42,59	30,82
225	12,11	43,7	44,19	39,12	35,39	25,49
246	5,07	67,09	27,84	7,02	48,38	44,59
254	5,19	71,01	23,8	5,41	57,72	36,87

TABLE B-5 HEAVY METAL CONCENTRATIONS IN BOTH REACTORS mg/L

	FE		CU		CD		NI		ZN	
Days	RR	SP	RR	SP	RR	SP	RR	SP	RR	SP
244	6.156	1.622	0.014	0	0,023	0,028	0,073	0,158	0,688	0,123
245[a]	2317	2374	1094	1093	105	103	1461	1490	1067	856
245	905	1436	340	523	50	74	681	994	519	579
247	404	448	111	52	31	31	448	559	348	282
250	170	166	28	13	15	8	304	283	197	119
252	77	44	5	-	9	-	206	156	122	50
254	39.45	27,65	11,20	3,4	2,83	3,21	117,5	77,88	28,98	25,63
257	19.85	-	9,7	1,225	2,47	1,575	65.125	72,63	18,12	-
259	14.15	16,75	9,695	0,54	2,125	1,185	54,93	62,7	15,1	12,85
261	17,12	14,28	13,57	1,09	1,0375	0,855	26.11	52,86	7,375	10,475
264	11	6,4	13,54	0,702	0,854	0,272	15.91	22,41	4,02	4,16
266	-	9,6	-	0,854	-	0,332	-	28,73	-	5,3
268	25	-	12,8	-	1,06	-	15,45	-	5,24	-
271	24,32	10,13	8,107	1,457	1,208	0,234	9,38	14,28	6,27	3,52
273	30,81	-	6,435	0,576	0,799	0,191	7,74	14,85	5,3	2,75
275	29	3,325	2,579	0,356	0,188	0,125	3,75	-	2,67	1,428
280	50,45	6,831	3,211	1,018	0,179	0,118	2,57	-	1,77	-
285	47,89	6,101	1,467	0,939	0,087	0,093	1,075	6,165	1,455	1,28
296	33,95	8,389	1,376	0,721	0,079	0,041	2,265	8,21	1,535	0,965
307	17,17	7,672	1,414	0,44	0,011	0,079	3,265	7,545	1,675	0,465

[a] initial loaded concentrations into the reactors

APPENDIX C

TABLE C-1 TURKISH HAZARDOUS WASTE CONTROL REGULATION

Appendix-12

ADMISSIBLE LIMITS OF HAZARDOUS WASTE CONCENTRATIONS FOR SANITARY LANDFILLING

HAZARDOUS WASTE	THRESHOLD VALUE
Acids	100 gr/ton municipal solid waste
Heavy Metals	100 gr/ton municipal solid waste
Zn	100 gr/ton municipal solid waste
Cu	100 gr/ton municipal solid waste
Na	100 gr/ton municipal solid waste
Cr^6	100 gr/ton municipal solid waste
Pb	100 gr/ton municipal solid waste
Cd	10 gr/ton municipal solid waste
Hg	2 gr/ton municipal solid waste
As, Se	1 gr/ton municipal solid waste
Cyanide	1 gr/m^3 municipal solid waste/day
Phenol	5 gr/m^3 municipal solid waste/day
Oils/ Carbohydrates	100 gr/ton municipal solid waste
TOC	10 gr/m^3 municipal solid waste/day

APPENDIX D

Table D.1 Mass Calculations for the Recycle Reactor

Days	Removed amounts from the system									Measured sulfide	Requried for total metal precipitation	sulfide from sulfate reduction
	Fe (mg)	Cu (mg)	Cd (mg)	Ni (mg)	Zn (mg)	SO_4^{-2} (mg)	SO_4^{-2} %	CO_3^{-2} (mg)	PO_4^{-3} (mg)	S^{-2} (mg)	S^{-2} (mg)	S^{-2} (mg)
247	1933	989	76	1035	736	4732	46	1687	18,54	1,52	2540	1577
254	2278	1083	102	1344	1038	8342	81	950	22,03	0,8	3117	2780
307	2299	1093	105	1457	1065	10242	100	234	5,18	2,64	3208	3414

Table D.2 Mass Calculations for the Single Pass Reactor

Days	Removed amounts from the system									Measured sulfide	Requried for total metal precipitation	sulfide from sulfate reduction
	Fe (mg)	Cu (mg)	Cd (mg)	Ni (mg)	Zn (mg)	SO_4^{-2} (mg)	SO_4^{-2} %	CO_3^{-2} (mg)	PO_4^{-3} (mg)	S^{-2} (mg)	S^{-2} (mg)	S^{-2} (mg)
247	2061	1057	82	1099	659	6104	58	2160	32,02	1,44	2619	2035
254	2333	1088	98	1373	818	6644	63	2171	32,43	0	3060	2214
307	2371	1093	103	1487	856	10394	99	1998	32,07	0,64	3159	3464