CHAPTER 2

LITERATURE REVIEWS

2.1 Backgrounds

Thailand produced nearly 22 million tons of waste annually (PCD, 2001). Municipal solid waste, which is made up of everyday waste produced by households and businesses, made up 67 percent of the total waste generation. While non-hazardous waste produced by industries accounted for 27 percent (PCD, 2001). The remainder of the waste, though produced in lower volumes, is potentially more dangerous due to its hazardous or infectious properties. This includes infectious waste from hospitals and hazardous waste from industries and communities. Generally, average amount of solid waste produced per person in 2002 was 0.65 kg per day. This number has grown estimated 17 percent between 1994 and 2001 despite reduced consumption during and immediately after the 1997 financial crisis. On average, urban areas in Thailand produce up to three times more (0.5-1.7 kg/person/day) than rural area's (0.4-0.6 kg/person/day). This is mostly due to higher concentration of businesses and other activities in urban centers. Data on waste generation and waste composition in Thailand in 2002 is shown in Table 2.1 and 2.2, respectively.

Solid waste generation is a fact of modern living. Everyone contributes to the problem. Most residents take solid waste collection and disposal at low cost for granted. Solid wastes may be defined as useless, unused, unwanted or discarded material in solid form. Semisolid food wastes and municipal sludge may also be included in municipal solid waste.

Municipal solid waste (MSW) includes wastes such as durable goods, nondurable goods, containers and packing, food wastes, yard wastes, and miscellaneous inorganic wastes from residential, commercial, institutional, and industrial sources.

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Table 2.1 Waste Generation in Thailand in 2002 (PCD, 2001)

Type of waste	Waste Generation (' 000th tons/yr)	Total minus reuse and recycling	Largest-producing provinces (% of total)
Municipal Solid Waste	14,400	12,800	Bangkok (27%) Nakhon Ratchasima (3.3%) Samut Prakan (2.3%) Khon Kaen (2.1%)
Infectious Waste	21.3	21.3	Bangkok (21%) Chiang Mai (3.9%) Nonthaburi (3.4%) Nakhon Ratchasima (3.0%)
Industrial Hazardous Waste	963	788	Samut Prakan (19%) Bangkok (18%) Pathumthani (11%) Samut Sakhon (7.0%)
Industrial Non-Hazardous Waste	5,890	1,271	Samut Prakan (13%) Bangkok (11%) Samut Sakhon (8.5%) Pathumthani (5.2%)
Community Hazardous Waste	372	182	Bangkok (34%) Nakhon Pathom (2.6%) Nonthaburi (1.4%) Pathum Thani (0.8%)

Examples of waste from these categories include appliances, newspapers, clothing, food scraps, boxes, disposable tableware, office and classroom paper, wood pallets, and cafeteria wastes.

MSW does not include wastes from sources such as municipal sludges, combustion ash, and industrial nonhazardous process wastes that might also be disposed of in municipal waste landfills or incinerators. Large quantities of solid wastes are also generated from many sources other than MSW. These quantities, although generated away from urban areas, or collected separately from municipal wastes, are enormous.

Table 2.2 Waste Composition in Thailand (PCD, 1998)

Types of Waste	Major Sources	Major Constituents
Municipal Solid Waste	Residential Commercial/Tourism Agriculture	Kitchen Waste (51%) Plastic and Foam (22%) Paper (13%) Glass (3%)
Infectious Waste	Hospitals (93%) Educational and labs (7%)	Tissue samples Blood and other liquids Surgical wastes and syringes
Industrial Hazardous Waste	Metals industries(33%) Electronic industries (28%) Plastic industries (8%) Chemicals and Petroleum industries (7%)	Filter materials, waste sludge (35%) Fuel, oil and grease (28%) Liquid organic compounds (8%)
Industrial Non-Hazardous Waste	Metals industries(36%) Food industries (13%) Furniture (7%)	Metals and metal alloys (30%) Parts of wood (16%) Animal parts (13%)
Community Hazardous Waste	Automotive stations (54%) Residential (19%) Agriculture (10%) Gas station (10%)	Recyclable waste oils (27%) Lead acid batteries (21%) Other toxic chemical (8%) Other waste oils (6%)

These solid waste sources are industrial, agricultural, mining and animal wastes. The industrial wastes are generally particular to the individual industry. They may include scrap metals, lumber, plastics, bales of waste paper, boards and rags, used-up drums and containers, slags, sludges, etc. The agricultural wastes consist of residues from most crop harvestings, horticulture wastes and orchard prunings. The animal wastes are generated from feedlots, dairies, chicken ranches, pig factories and other confined animal raising operations. The waste is generally manure, bedding material, punch manure from slaughterhouses, and carcasses. The major components of mining wastes are the by-products of mining operations and processing of minerals and fossil fuels. Hazardous wastes include explosive, flammable, volatile, radioactive, toxic, and pathological wastes. These wastes require special care in storage, collection, transportation, treatment, and disposal to prevent harm to human health, animals, and property. These wastes can increase serious irreversible or incapacitating illness, or pose potential hazards to human health or environment when improperly managed.

Today, solid waste is accepted as a major problem of our society. Many waste disposal sites in Thailand are sources of environment pollution because waste is still largely disposed of without effective safety and environmental control measures. This situation poses a serious risk to the environment and to human health, especially via the path of groundwater contamination.

Landfills are the most widely used method of solid waste disposal in Thailand and the world today. This is primarily due to their ability to be designed, installed and operated at lower costs than other solid waste management alternatives. However, landfills have often been designed and operated without an appropriate understanding of their consequences within a particular environmental setting. Indeed, few other waste management systems afford so little opportunity for operational control as the indigenous processes of waste stabilization proceed.

2.2 Principles of Decomposition in landfill

Solid wastes deposited in landfills decompose by a combination of chemical, physical, and biological processes. The decomposition produces solid, liquid, and gaseous byproducts, all of which may be of concern in the overall management of a landfill. The biological processes acting on the organic materials within the refuse commence soon after refuse placement. However, interdependencies among the three processes require that chemical and physical processes also be considered along with biological processes.

Physical decomposition of solid waste results from the breakdown or movement of the refuse components by physical degradation and by the rinsing and flushing action of water movement. Upon reaching field capacity (the moisture level beyond which any increases in moisture will drain by gravity), flow of dislodged refuse particles occurs as a result of pressure gradients, and diffusion as a result of concentration gradients. As the moisture level of the refuse increases, additional refuse particles are dislodged (Chain and DeWalle, 1997).

Chemical processes resulting in refuse decomposition include the hydrolysis, dissolution/precipitation, sorption/desorption, and ion exchange of refuse components. Chemical decomposition generally results in altered characteristics and greater mobility of refuse components, thereby enhancing the rate at which the landfill becomes more chemically uniform (Chain and DeWalle, 1997).

Although both physical and chemical decomposition of refuse materials are important in landfill stabilization, biological decomposition is the most important process. Specifically, biological decomposition is the only process that produces methane gas (Chain and DeWalle, 1997).

Biological decomposition occurs with naturally present bacteria. It is a complex process within landfill sites, consisting of various biologically mediated sequential and parallel pathways by which refuse is decomposed to various end products.

The products of the physico-chemical and biological and biological decomposition processes are depicted on Figure 2.1.

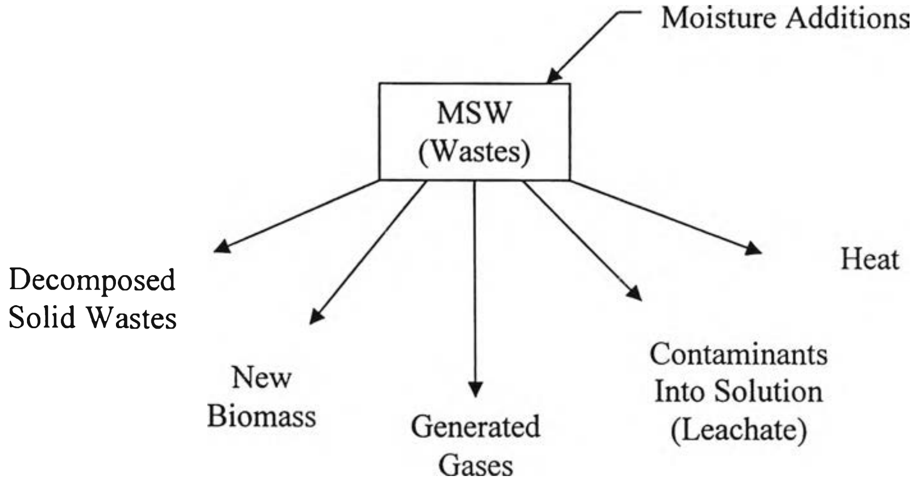


Figure 2.1 Byproducts of solid waste decomposition (Chain and DeWalle, 1997)

2.2.1 Landfill as a biochemical reactor

As a result of combination of processes referred to in Section 2.2, landfill is a form of biochemical reactor, similar to an anaerobic digester in a wastewater treatment plant. Of course, there are potentially important limitations on the degree to which the landfill contents are mixed. The result is variabilities in such features as moisture, refuse age, and composition in various locations within the refuse. Thus, knowledge of moisture content, leachate characteristics, and migration of the gas within refuse are essential to understanding the rate and current status of the decomposition processes.

Biological decomposition takes place in three stages, each of which has its own environmental and substrate requirements that result in characteristic end products (Chain and DeWalle, 1997).

1. Aerobic Decomposition

Aerobic processes require the presence of oxygen. Thus, aerobic decomposition occurs on initial placement of the refuse, while oxygen is still available. Aerobic decomposition may continue to occur on, and just below, the surface of the fill, as well. However, because of the finite amount of available oxygen buried within the refuse and the limitations on air transport into the fill, aerobic decomposition is responsible for only a small portion of the biological decomposition within the refuse.

During this first stage of decomposition, aerobic microorganisms degrade organic materials to carbon dioxide, water, partially degraded residual organics, and considerable heat. Aerobic decomposition is characteristically rapid, relative to subsequent anaerobic decomposition, and the oxygen demand of this refuse is high. A general relation for this decomposition is

Degradable waste +oxygen → CO_2 + H_2O+ biomass+heat + partially degraded materials

2. Acid-Phase Anaerobic Decomposition (Nonmethanogenic)

The second stage of refuse decomposition involves facultative microorganisms that become dominant as the oxygen is depleted. These microorganisms continue the decomposition processes. In this, the acid or acetogenic phase, high concentrations of organic acids, ammonia, hydrogen, and carbon dioxide are produced. Acid fermentation prevails, with characteristic end products being high levels of carbon dioxide, partially degraded organics (especially organic acids) and some heat, as described by the following equation:

Degradable waste → CO_2 + H_2O+ organism growth+ partially degraded organics

The production of carbon dioxide (high partial pressure) and large amounts of organics acids result in the lowering of the pH of the leachate to the range of 5.5 to

6.5, which in turn causes the dissolution of other organics and inorganics. The result is a chemically aggressive leachate with high specific conductance.

3. Anaerobic Decomposition (Methanogenic)

As the biodegradation of the refuse progresses, the oxygen becomes depleted, the redox potential is reduced, and the third stage of refuse decomposition involving the anaerobic methanogenic bacteria become dominant. These organisms produce carbon dioxide, methane, and water, along with some heat. Characteristically, these organisms work relatively slowly but efficiently over many years to decompose remaining organics.

The methanogenic bacteria utilize the products of the anaerobic acid stage, for example, hydrogen,

$$4H_2O + CO_2 \rightarrow CH_4 + H_2O$$

and acetic acid,

$$CH_3COOH \rightarrow CH_4 + CO_2$$

Consumption of the organic acids raises the pH of the leachate to the range of 7 to 8. Consequently, the leachate becomes less aggressive chemically and possesses a lower total organic strength. Organic acids that cannot be used directly by bacteria are converted to methane by an intermediate step. Volatile fatty acids act as a substrate for methanogenic bacteria, but high concentrations inhibit the establishment of a methanogenic community and at very high concentrations are toxic.

The methane bacteria that function in the methanogenic stage obtain energy from two reactions: (1) the reduction of CO_2 through the addition of H_2 to form CH_4 and H_2O and (2) the cleavage of the CH_3COOH into CH_4 and CO_2. Although energy is captured by the microorganisms during this stage, very little synthesis of new cell material occurs (McCarty, 1963).

The time required for the methanogenic stage to commence may be from six months to several years after placement. The shorter time period is associated with situations of higher water content and flow rate. It is not worthy; however, that instability in the system or rapid variations in water movement may inhibit the methanogenic bacteria.

During the methanogenic phase, leachate characteristically has a near-neutral pH, low volatile fatty acid content and low total dissolved solids (TDS). Small portions of the organic refuse, the ligand-type aromatic compounds, are slow to degrade anaerobically. These compounds are important factors in adsorption and complexation (Lu et al., 1984).

The methanogenic stage does not mark the end of hydrolysis and fermentation that occurs in the acetogenic stage. These steps continue, but the methanogenic bacteria population grows to a level at which the bacterial rate of consumption of the acetic stage end products approaches the rate of production.

2.3 Phases of Landfill Stabilization

Most landfills proceed through a series of rather predictable events which are influenced by climatological conditions, operation variables, management options and control factors operative in the landfill environment (Pohland et al., 1983). These events can be observed by monitoring certain leachate and gas parameters which serve to describe the following phases of stabilization:

Phase I: Initial Adjustment

This period prevails from initial waste placement through the closure of the landfill segment and to the time when environmental parameters first reflect the onset of stabilization processes. Incipient aerobic decomposition consumes oxygen and produces carbon dioxide.

Phase II: Transition

During this period, field capacity is exceeded and regular leaching begins. The oxygen entering the landfill with the waste is depleted and a transition from aerobic to anoxic and anaerobic conditions occurs. During this transition, the primary electron acceptor shifts from oxygen to nitrate and sulfate and then to carbon dioxide. Reducing conditions are established and intermediates such as volatile organic acids first appear in abundance.

Phase III: Acid Formation

The third phase is the period when significant amounts of volatile organic acids are produced by the continuing hydrolysis and fermentation of waste and leachate constituents. The accumulation of high quantities of volatile acids results in pH depression. Mobilization and complexation are found to be the principal mechanisms for increasing concentrations of heavy metal species in the leachate. Essential nutrients, nitrogen and phosphorus are released from waste and utilized at a rate commensurate with biomass development. Hydrogen gas is also produced and influences microbial metabolism and the types of intermediary products being form (Chian and DeWalle, 1976).

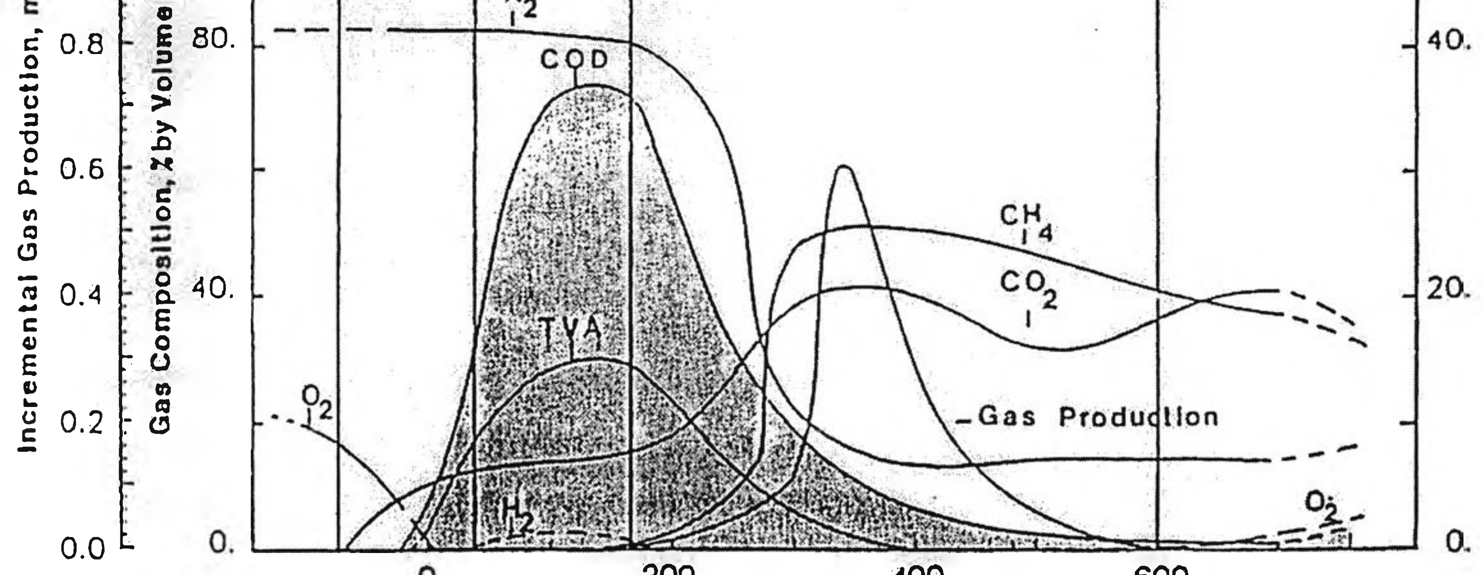
Phase IV: Methane Fermentation

During this period, the intermediate products are converted to methane and excess carbon dioxide by the methane forming organisms. The pH of leachate increases to neutral as the volatile organic acids are converted principally to methane and carbon dioxide, and carbonate-bicarbonate buffer system is again re-established. Oxidation-reduction potentials in the Methane Fermentation phase are highly negative and are indicative of highly reducing condition (Stratakis, 1991). Removal of heavy metals from leachate by precipitation and complexation with sulfide and carbonate anions proceeds. Excess sulfates and nitrates are reduced to sulfides and ammonia (Pohland, 1975). Leachate organic strength, as measured by chemical oxygen demand

(COD), biochemical oxygen demand (BOD_5), and total organic carbon (TOC), drastically decreases as a result of volatile acids consumption. The methane percentages, as well as the rate of gas production are at their highest during this period.

Phase V: Final Meturation

This period follows active biological stabilization of the readily available organics in the waste and leachate. Nutrients may become limiting, measurable gas production creases, oxidation-reduction potential may slowly rise as more oxidizing conditions are reestablished, and the more resistant organics may slowly degrade and influence mobility of other species.


Incremental Gas Production, m
Gas Composition, % by Volume
0.8
0.6
0.4
0.2
0.0
80.
40.
0.
40.
20.
0.
2
COD
TVA
H_2
O_2
CH_4
CO_2
Gas Production
O_2
0
200
400
600

2.4 Factors Affecting Landfill Stabilization

Microbially-mediated waste stabilization in landfills, as in separate anaerobic digestion processes, is affected by a number of factors such as pH, temperature, availability of nutrients, the presence of inhibitory substances, moisture content, and preprocessing techniques. The effects that such variables have on stabilization processes usually manifest themselves in terms of leachate and gas characteristics throughout the active life of the landfill.

pH, a measurement of hydrogen ion concentration, is a crucial parameter in anaerobic waste conversion. The normal operational range is 6.5 to 7.6, with an optimum pH between 7.0-7.2 (Perkin and Owen, 1982; McCarty, 1964). The pH of an anaerobic system is a function of both volatile organic acids and alkalinity concentrations, as well as the partial pressure of carbon dioxide evolved during stabilization (McCarty and Smith, 1986). During the Acid Formation phase, the carbonate-bicarbonate alkalinity buffer system is displaced by the volatile acid buffer system, resulting in a reduction in pH (Stratakis, 1991). This reduction to low pH does not only affect the rates of hydrolysis, liquefaction, and gas production, but also encourages mobilization of heavy metals which may be capable of inhibiting the overall conversion process (Pohland et al., 1983).

Temperature, anaerobic processes usually function in either mesophilic (30 to 38 °C) or thermophilic (50 to 60 °C) temperature ranges (Kotze, et al., 1969). Ham and coworkers (1983) studied the rate of methane generation from solid waste within the temperature range of 21 to 48°C and indicated that the optimum range was 41°C. The optimum temperature ranges for mesophilic anaerobic digestion reported by McCarty is 30-32°C (Torien, et al., 1967). Parkin and Owen (1982) recommended that a temperature as close to 35°C as possible be maintained during anaerobic process start-up and recovery from upset. Regardless of operational temperatures chosen, consistency of temperature is considered to be important for maximizing stabilization process performance. Nevertheless, temperature fluctuation in landfills is expected, since landfill temperature is not regulated and usually exhibits the influence of atmospheric temperature and insulation provided by surrounding cells as well as cover layers.

Adequate supplies of nutrients, macronutrient, nitrogen and phosphorus, are needed in larger amounts, whereas micronutrients such as iron, nickel, cobalt, sulfur, calcium, molybdenum, tungsten, selenium, and some organics are required in minute quantities for bacterial cell maintenance and synthesis (Chian and DeWalle, 1977). Nitrogen is needed for the production of protein, enzyme, ribonucleic acid (RNA), and deoxyribonucleic acid (DNA). Phosphorus is used to synthesize energy-storage compounds (adenosine triphosphate-ATP) as well as RNA and DNA. Chian and DeWalle concluded that the upper limits of leachate COD: P and COD: N was 4,360: 1 and 39:1, respectively. However, a COD: P ratio of 2,200:1 was determined sufficient for anaerobic digestion of fatty acids by McCarty and Speece (1963).

The presence of inhibitory substances is another concern. Conditions such as accumulation of volatile organic acids, high concentrations of ammonia nitrogen, sulfide, and heavy metals, or the presence of toxic substances are common causes of failure in many anaerobic digester operations. The extent of toxicity of each substance is associated with concentrations and forms, contact time, as well as acclimation ability of microbial consortia.

Ammonia is normally the decomposition product of urea or protein. Ammonia, a source of nitrogen for anaerobic bacteria, is stimulatory to the biological reactions. However, at high concentrations, it may be detrimental to microorganisms. Soluble ammonia gas, which constitutes the majority of ammonia nitrogen at a pH higher than 7.2, is inhibitory at considerably lower concentrations than the ammonia ion. Inhibitory effects have been observed for ammonia nitrogen concentrations of 1,500 mg/L, and concentrations above 3,000 mg/L have caused termination in gas production regardless of pH (Pohland et al., 1993).

Sulfide in anaerobic treatment originates from the reduction of sulfate or sulfur-containing inorganic compounds or the introduction of sulfide with wastes.

Sulfides in soluble form have been reported to cause cessation in gas production at concentrations in excess of 200 mg/L, while concentrations of soluble sulfide varying from 50 to 100 mg/L can be tolerated in anaerobic treatment with little or no acclimation required (Parkin and Owen, 1982). The presence of heavy metals such as iron can lesson this effect, since metal sulfides can be formed and easily removed from solution by precipitation.

Small concentrations of heavy metals are necessary for proper functioning of bacterial enzyme systems. On the other hand, excess concentrations may lead to damage due primarily to the binding of metals with functional groups on proteins or replacing naturally occurring metals in enzymes. Heavy metals can combine with sulfide, carbonate, or hydroxide to form precipitates. Nonetheless, their mobility is also dependent on pH and the extent of sorption and desorption, ion exchange, as well as chelation reactions taking place within refuse mass. Usually, only heavy metals that exist in free cation forms at concentrations above threshold are harmful to microbial life (Mosey, 1963).

Although stabilization process may be impaired by some types of organic substances, e.g., chlorinated hydrocarbons, studies by Pohland (1983) indicated that finite amounts of halogenated organic compounds can be detoxified in landfill environments through reductive dehalogenation reactions. Yet, chloroform has been found to be extremely toxic, even at a concentration as low as 0.5 mg/L, and was a cause of inhibition in a number of anaerobic waste treatment plants in England.

Moisture content is considered important in anaerobic waste stabilization processes, since most physical and biochemical reactions occur in liquid phase or at the interface between phases (Chian et al., 1977). Liquid also serves as a transport medium for microorganisms and substrate, providing contact opportunity for reactions to proceed. Sufficient moisture content is critical for rapid stabilization within landfills, and the optimum ranges for maximum methane production were observed by Dewalle and coworkers (1976) to vary between 60 and 78%. Typically, 25% moisture is a lower limit required for decomposition to begin (Yaron et al., 1984).

Major sources of moisture in landfill are from rainwater or snowmelt infiltrating final covers, water entering with solid waste, and water contained in various types of cover materials.

Distribution of moisture is also an important aspect. In a system with good moisture distribution, longer contact time between microorganism and substrate as well as greater amounts of accessible substrate are expected, resulting in higher waste conversion efficiency. This is evident for landfills where leachate recirculation is employed, since this technique is realized to promote a more thorough distribution of moisture throughout the refuse mass (Pohland and Harper, 1986; Pohland, 1980; Leckie et al., 1979).

Mechanical volume reduction methods include shredding, milling, and grinding decreases the size of solid waste materials and increases the surface areas where bacteria can attach and proliferate, thus aiding in decomposition processes (Stratakis, 1991). Baled solid waste tends to retard the flow of water and may cause uneven distribution of moisture, leading to less complete and slower biodegradation (Pohland et al., 1985). Sorting and recycling divert nonbiodegradable portions of the solid waste, minimize channeling and short-circuiting and maximize effective exploitation of landfill space.

2.5 Indicator Parameters Descriptive of Landfill Stabilization

There are certain traditional indicator parameters that can be used to indicate and to describe the presence, intensity, and longevity of each phase of landfill stabilization. Both gas and leachate parameters are monitored and analyzed for this purpose.

Chemical oxygen demand (COD) is a chemical parameter indicative of the organic strength of leachate in terms of the amounts of oxygen needed to obtain oxidation of the chemically oxidizable fractions contained within the waste. The concentration of volatile organic acids (VOA) is closely related to the biodegradability portion of the leachate constituents, since during the Acid Forming phase, the majority of the COD is composed of VOA. pH and oxidation-reduction potential (ORP) are physical-chemical parameters and indicative of the oxidation-reduction and acid-base condition, respectively. Availability of essential nutrients, nitrogen and phosphorus, are assessed through the analyses of leachate ammonia nitrogen and orthophosphate, which are the readily available forms of both elements (Chian and DeWalle, 1976).

The abundance of methane, carbon dioxide, nitrogen, and oxygen in landfill gas is also characteristic of stabilization. Therefore, when considered along with a aforementioned parameters, the manifestation of gas production during the predominant stabilization phase (Phase IV) is obtained. Gas production data are also used to evaluate the extent of waste transformation as organics are converted to carbon dioxide and methane.

The intensity of these parameters is dependent upon the prevailing phase of landfill stabilization and is also influenced by operational management strategies, i.e., moisture management, buffer addition, and removal of inhibitory compounds; the nature of the wastes; and closure and post-closure methods eventually applied (Pohland et al., 1993).

2.6 Leachate Generation

When rainfall falls on a landfill site, the resulting water either will be shed from the fill as stormwater runoff, evaporate, transpire under the action of surface vegetation, or infiltrate into the landfill to create leachate. Leachate that infiltrates into the landfill either is stored, absorbed by the landfilled material or it migrates through the landfill under the force of gravity, ultimately being intercepted by the liner system. The amount of leachate generated at a landfill depends on many conditions, including site climate, landfill morphology, waste depth, landfill surface conditions, and the operation of the facility. The prediction of the amount of leachate that is

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produced at a given landfill is generally estimated by performing a water budget analysis.

2.7 Characteristics of Leachate

The characterization of leachate provides important information necessary for the control of landfill functions and for the design and operation of leachate treatment facilities, facilitates risk analysis of leachate impact on the environmental should liners leak, permits comparison of the impact of alternative landfill design or operating protocol on the environment, and discloses the interaction of leachate parameters.

Material is removed from the waste mass via mechanisms that include leaching of inherently soluble material, leaching of soluble products of biological and chemical transformation, and washout of fines and colloids. The characteristics of the leachate are highly variable depending on the composition of the waste, rate of water infiltration, refuse moisture content, and landfill design, operation, and age. These variations are demonstrated in Table 2.3, where ranges in concentrations of significant leachate components are presented as a function of stabilization phase.

Organic containments of leachate are primarily soluble refuse components or decomposition products of biodegradable fractions of waste. Organic compounds detected in nineteen MSW landfill leachates or contaminated groundwater plumes emanating from landfills included organic acids, ketones, aromatic compounds, chlorinated aromatic compounds, ethers, phthalates, halogenated aliphatic compounds, nitro-aromatic compounds, phenols, heterocyclic compounds, pesticides, sulfur substituted aromatic compounds, polyaromatic hydrocarbons, polychlorinated biphenyls, and organophosphates (Brown and Donnelly, 1988).

Table 2.3 Landfill leachate concentration ranges as a function of degree of landfill stabilization (Reinhart and Townsend, 1997)

Parameter	**Phase II Transition**	**Phase III Acid Formation**	**Phase IV Methane Formation**	**Phase V Final Maturation**
BOD, mg/L	100-10,000	1,000-57,000	600-3,400	4-120
COD, mg/L	480-18,000	1,500-71,000	580-9,760	31-900
TVA, mg/L as acetic acid	100-3,000	3,000-18,000	250-4,000	0
BOD/COD	0.23-0.87	0.4-0.8	0.17-0.64	0.02-0.13
NH_3-N	120-125	2-1,030	6-430	6-430
pH	6.7	4.7-7.7	6.3-8.8	7.1-8.8
Conductivity, µmhos/cm	2,450-3,310	1,600-17,100	2,900-7,700	1,400-4,500

The class of organic compounds found at highest concentration in leachates is generally VOAs produced during the decomposition of lipids, proteins, and carbohydrates (Albaiges et al., 1986; Schultz and Kjeldsen, 1986). Aromatic hydrocarbons, including benzene, various xylems, and toluene, are also frequently found at lower concentrations (Schultz et al., 1983). These compounds were considered to be constituents of gasoline and fuel oils. Sawney and Kozloski (1984) reported that the presence of the more soluble, less volatile aromatic components of gasoline in the leachate suggested that the more volatile components were being gas stripped from the landfill. Nonvolatile classes of compounds such as phenolic compounds may be degradative byproducts of lignin. A small complex fraction found in several leachates contained nicotine, caffeine, and phthalate plasticizers (Albaiges et al, 1986).

The dominant organic class in leachate shifts as the age of the landfill increases due to the ongoing microbial and physical/chemical processes within the landfill. An investigation of leachates obtained from landfills operated from one to 20 years found that the relative abundance of high molecular weight humic-like substances decreases with age, while intermediate-sized fulvic materials showed significantly smaller decreases (Chian, 1977). The relative abundance of organic compounds present in these leachates was observed to decrease with time in the following order: free VOAs, low molecular weight aldehydes and amino acids, carbohydrates, peptides, humic acids, phenolic compounds, and fulvic acids.

A variety of heavy metals are frequently found in landfill leachates including zinc, copper, cadmium, lead, nickel, chromium, and mercury (Lu et al.,1985). Again, these metals are either soluble components of the refuse or are products of physical processes such as corrosion and complexation. In several instances heavy metal concentrations in leachate exceed U.S. Toxicity Characteristic Leaching Procedures standards.

Heavy metal concentrations in leachate do not appear to follow patterns of organic indicators such as COD, BOD, nutrients, or major ions (Lu et al., 1985). Heavy metal releases is a function of characteristics of the leachate such as pH, flow rate, the concentration of complexing agents.

2.7.1 Young Leachate

In the first few years, leachates contain the readily biodegradable organic matter. Thus these young leachates tend to be acidic due to the presence of volatile fatty acids. The pH is typically in the range of 6 to 7 and may be lower in stress (dry) landfills. The young leachates are derived from processes such as the complex biodegradation of organics (e.g. cellulose) and simple dissolved organics (e.g. organic acids).

The result of these actions is that chemical concentrations are generally in the ranges indicated in Table 2.4. Typical values of sewage and groundwater concentrations are provided for comparison.

With time, leachates become simple dissolved organics (e.g. gases CH_4, CO_2, H_2, $H_2 O$, and biomass) and decrease in strength.

Table 2.4 Typical chemical concentrations in young landfill leachate (Chian and DeWalle, 1977)

Parameter	Leachate concentration (mg/L)	Typical sewage concentration (mg/L)	Typical groundwater concentration (mg/L)
COD	20,000-40,000	350	20
BOD_5	10,000-20,000	250	0
TOC	9,000-15,000	100	5
VOA	9,000-25,000	50	0
NH_3 -N	1,000-2,000	15	0
Org-N	500-1,000	10	0
NO_3-N	0	0	5

2.7.2 Old Leachate

Table 2.5 Typical chemical concentrations in older leachate

Parameter	Concentration (mg/L)
COD	500-300
BOD_5	50-100
TOC	100-1,000
Volatile fatty acids such as acetic acid	50-100

After 4 to 5 years, the pH increases to the range of 7 to 8. The changes occur as a result of depletion of the readily biodegradable organics and the production of gases. The poorly biodegradable organics remain. Typical chemical concentrations are provided in Table 2.5. Nitrogen levels are very useful as indicators of the age of the leachate. Ammonia nitrogen (NH_3- N) and organic nitrogen (Org-N) are produced by the decomposition of organics and are stable in the anaerobic environment; nitrate nitrogen (NO_3-N) is consumed in the anaerobic environment (Chian and DeWalle, 1977). These trends are demonstrated in Table 2.6

Table 2.6 Nitrogen constituent concentrations for various sources (Chian and DeWalle, 1977)

Sample	Age (yr)	NH_3 -N (mg/L)	Org-N (mg/L)	NO_3 -N (mg/L)
Sewage	-	15	10	0
Groundwater	-	0	0	5
Young leachate	1	1,000-2,000	500-1,000	0
Several sites				
(Germany)	12	1,100	-	-
Du Page Co. (Illinois)	15	860	-	-
Rainham (U.K.)	24	17	-	-
Waterloo (Canada)	35	12	-	-

2.8 Heavy Metals

2.8.1 Nickel chemistry

Nickel (Ni) is the third element in Group VIII in the periodic table. It has an atomic number of 28, with an atomic weight of 58.69 g/mol. Nickel ion commonly occurs with a valence of 2 (divalent cation, Ni^{+2}) rather than 1,3, or 4. Ni^{+2} is natural aqueous species. In reducing conditions, nickel would present in insoluble nickel sulfides. Nickel would form complexes with hydroxide, carbonates, and organic ligands in aerobic conditions.

Nickel and its compounds are widely used in various industries such as manufacture of rechargeable batteries, electronic components, coinage, enamel frits, ceramic glazes, stainless steels and other corrosion resistant alloys. They are used as catalysts in hydrogenation of fats and oils and paint pigments (Stokinger, 1991).

The main health concern is if workers are exposed to certain compounds of nickel. Direct contact to nickel and its compound can cause an allergic dermatitis. Inhaling gaseous nickel compound would cause acute effects such as headache, giddiness, nausea, and vomiting. Exposure to nickel-containing dust can also result in sensitization, conjunctivitis, pneumonitis, and asthma. An increased incidence of lung and nasal sinus cancer occurs in long-term exposure to some kinds of nickel ores (Stokinger, 1991).

2.8.2 Zinc chemistry

Zinc (Zn) is the first element in Group IIB in the periodic table; it has an atomic number of 30, an atomic weight of 65.38, and a valence of 2. The average abundance of Zn in the earth's crust is 76 ppm; in soils, 25 to 68 ppm; in streams, 20µg/L, and groundwaters, < 0.1 mg/L. The solubility of zinc is controlled in natural waters by adsorption on mineral surfaces, carbonate equilibrium, and organic complexes (Standard Methods for the Examination of Water and Wastewater, 1980).

Zinc is one of the most common elements in the earth's crust. It is present in nearly all foods. Also found naturally in air, soil, and water, it is commercially used to produce such products as dry cell batteries, brass, bronze, fungicides, and pigments. Zinc combines with elements such as chlorine, oxygen, and sulfur to form compounds. Some of the most familiar compounds are zinc chloride, zinc oxide, zinc oxide, zinc sulfate, and zinc sulfide. These substances are used by the drug industry as ingredients in common products like sun blocks, diaper rash ointments, and deodorants. Some zinc compounds also compounds also end up in residual waste and require management at hazardous waste treatment and disposal facilities. Zinc is an essential growth element for plants and animals but at elevated levels it is toxic to some species of aquatic life. The United Nations Food and Agriculture Organization recommended level of zinc in irrigation waters is 2 mg/L. The U.S. EPA secondary drinking water standard MCL is 5 mg/L. Concentrations above 5 mg/L can cause a bitter astringent taste and opalescence in alkaline waters (Standard Methods for the Examination of Water and Wastewater, 1980).

Zinc can negatively affect health in large doses. It results in such physical symptoms as stomach cramps and nausea. Ingesting high levels of zinc for several months may lead to anemia, damage to the pancreas, and decreased levels of cholesterol. It is not known if high levels of zinc affect the ability of woman to reproduce or cause birth defects in humans. Inhaling large amounts of zinc may cause a specific short-term disease called metal fume fever. Inhalation can occur from exposure to zinc dust, or smelting or welding fumes. However, very little is known about the long-term effects of breathing zinc dust or fumes. Consuming too little zinc is also a concern. Without enough zinc in the diet, people may experience loss of appetite, decreased sense of taste and smell, impaired immune function, slow wound healing, or skin sores.

2.9 Heavy metals Removal

There are a number of technologies available for the removal of heavy metals from a wastewater. Chemical precipitation is most commonly employed for most of the metals. Common precipitants include OH^-, $CO_3^{2-}$and S^{2-}. Metals are precipitated as the hydroxide through the addition of lime or caustic to a pH of minimum solubility. Metals can also be precipitated as the sulfide or in some cases as the carbonate. Sulfide precipitation has several potential advantages as an alternative to hydroxide precipitation. The solubilities of metal sulfides, shown in Figure 2.3 are lower than those of corresponding metal hydroxides.

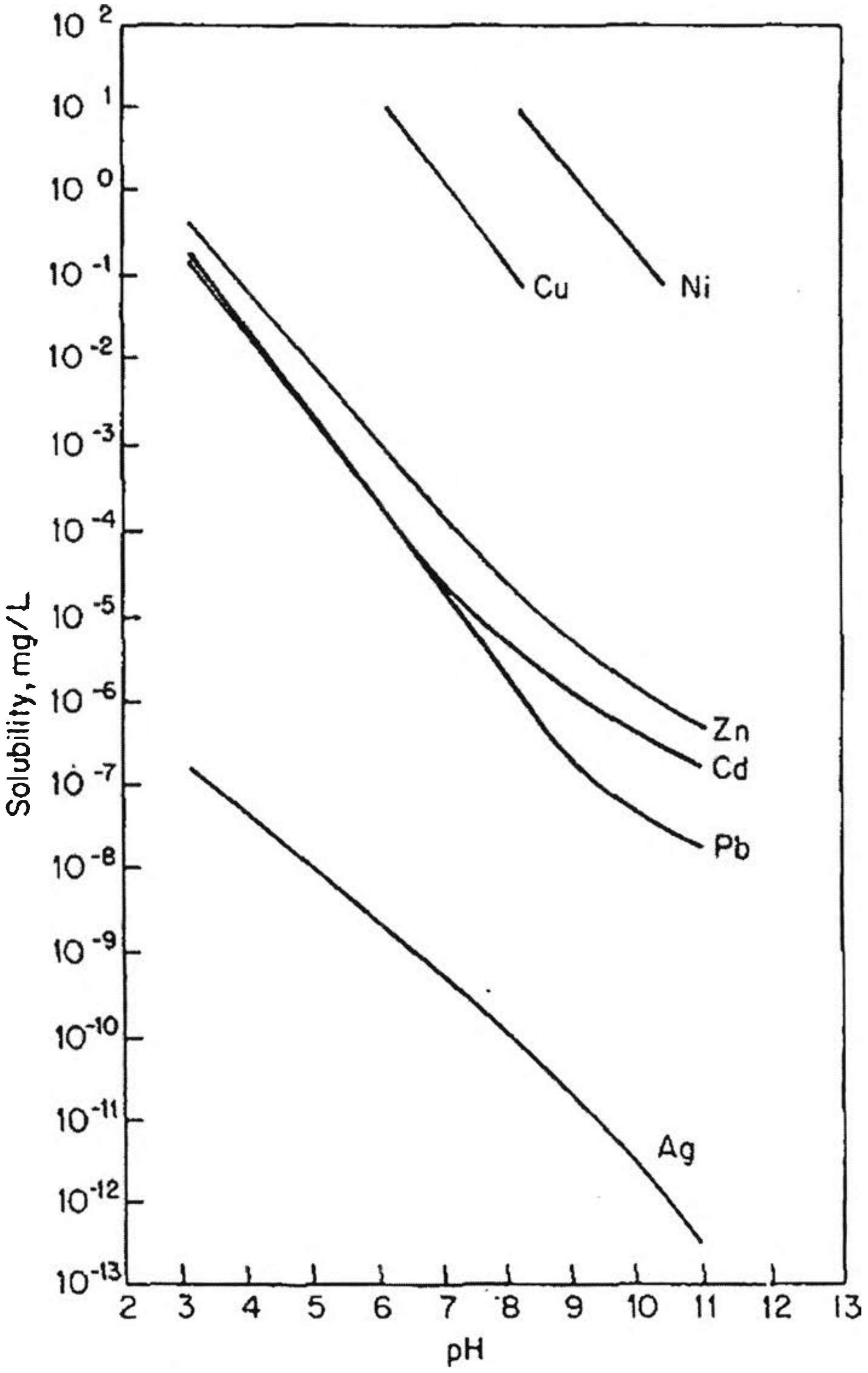

Figure.2.3 Solubilities of metal sulfides as a function of pH (Freeman, 1989)

2.9.1 Nickel Removal

Wastewaters containing nickel originate from metal-processing industries, steel foundries, motor vehicle and aircraft industries, printing, and in some cases, the chemicals industry. In the presence of complexing agents such as cyanide, nickel may exist in a soluble complex form. The presence of nickel cyanide complexes interferes with both cyanide and nickel treatment. Nickel forms insoluble nickel hydroxide upon the addition of lime, resulting in a minimum solubility of 0.12 mg/L at pH 10 to 11. Nickel hydroxide precipitates have poor settling properties. Nickel can also be precipitated as the carbonate or the sulfate associated with recovery systems. In practice, lime addition (pH 11.5) may be expected to yield residual nickel concentrations in order of 0.15 mg/L after sedimentation and filtration. Recovery of nickel can be accomplished by ion exchange or evaporative recovery, provided the nickel concentrations in the wastewaters are at a sufficiently high level.

The major attenuation mechanism of nickel includes sorption and precipitation. Janne (1968) found that nickel is removed from solution by hydrous metal oxide precipitates. Nickel appears to have much greater affinity for manganese oxide than ferric oxide. Korte et al. (1976) found that nickel retention in soil from a nickel-spiked municipal landfill correlates well with surface area, cation exchange capacity, and clay content. Other soil factors favoring retention of nickel include alkaline conditions, high concentrations of hydrous metal oxides, and free lime. The mobility of nickel is moderate in clayey soil (Griffin, 1977).

2.9.2 Zinc Removal

Zinc is present in wastewater streams from steelworks, rayon yarn and fiber manufacture, ground wood-pulp production, and recirculating cooling water systems employing cathodic treatment. Zinc is also present in wastewaters from the plating and metal-processing-industry. Zinc can be removed by precipitation as zinc hydroxide with either lime or caustic. The disadvantage of lime addition is the concurrent precipitation of calcium sulfate in the presence of high sulfate levels in the wastewater. An effluent soluble zinc of less than 0.1 mg/l has been achieved at pH 11.0.

The major attenuation mechanisms for zinc are adsorption, cation exchange, and precipitation. Zinc is a common cation in soil systems. As is true with other cations, the pH of the leachate-soil system is crucial factor in zinc removal, reflecting the influence of dominant hydrolysis species on both the affinity for soil colloids and the solubility of zinc (Gebhard, 1978).

The attenuation of zinc was found to increase rapidly for a pH change from 2 to 8 with a significant rise around 6 to 8 (Griffin et al., 1976). Precipitation of zinc with a variety of anions including sulfide, phosphate, carbonate, and silicate has also been found to be important in zinc immobilization (Stumm and Morgan, 1970; Fuller, 1977). Experimental results suggest that the removal of zinc is also dependent on clay type and cation-exchange capacity (Griffin, 1977; Farquhar, 1977). Organic matter improves zinc immobilization (Folett and Lindsay, 1971; Huang et al., 1977; Norcell, 1972), and zinc chelates are most stable at pHs between about 5 and 7.5 (Folett and Lindsay, 1971; Huang et al., 1977; Norcell, 1972). Soil material favoring attenuation of zinc includes clays, organic material, hydrous metal oxides, and free lime. Zinc attenuation will be most favored by an alkaline condition. In general, mobility of zinc in a clayey environment is low (Griffin, 1977).

2.10 Related Studies

Chain and DeWalle (1976) reported that the formation of metal sulfides under anaerobic conditions effectively eliminated the majority of heavy metals in leachate. In addition, neutral or above neutral leachate conditions, promoted by leachate recirculation, enhance metal hydroxide precipitation.

Pohland (1985) studied the management of hazardous wastes by landfill co-disposal with municipal refuse. Results of research investigations on codisposal of municipal and industrial wastes within landfills equipped with provisions for leachate containment and recycle have provided opportunities to examine the mechanisms of leachate formation, to characterize the phases of landfill stabilization, and to suggest strategies for landfill management at sites where codisposal of refuse with industrial wastes is practiced. Evidence from pilot-scale investigation utilizing municipal refuse and metal plating sludges in simulated landfills has provided insights into the assimilative capacity of the landfill for admixed heavy metal sludges and the possible mechanisms of impact on overall stabilization. At sludge levels that did not exceed this capacity (~0.01 kg/kg of refuse), normal stabilization occurred. At higher levels, inhibitory effects were clearly established with associated persistence of leachate contaminants, including the heavy metals.

Pohland (1986) investigaed 2-year pilot-scale on the codisposal of heavy metal sludge with municipal refuse, under the influence of leachate containment and recycles. The results are used to illustrate and describe the effects of various metal loadings on the normal progress of waste stabilization and to assess associated assimulative capacity. Evidence of metal precipitation as sulfides or hydroxides and subsequent removal by filtration and sorption in the refuse mass was demonstrated. Conversely, the mobilization of heavy of heavy metals was shown to be enhancing by complexation with humic-like substances.

Mott (1987) considered the precipitation in two landfill leachates. This investigation studied the partitioning of cadmium, copper, zinc, and nickel with iron and manganese solid phase formed from leachate constituents at pH 9. Two solid waste landfill leachates were studied in a preliminary study of in situ precipitated hydrous ferric and manganese oxides in the removal of heavy metals from aqueous solutions by sorption-co-precipitation. For the conditions studied, the zinc removal rate was greater than 95%, cadmium was 89-90%, copper was 70-75%, and nickel was 24-36%.

Pohland, et al. (1987) performed the fate of selected organic priority pollutants codisposed with municipal refuse in landfills. This was accomplished by operating four laboratory-scale simulated landfill cells under the influence of single pass leaching and leachate recycle throughout both the acid formation and methane fermentation phases of landfill stabilization. The organic pollutants added with the municipal refuse were chosen because of their association with wastes generated from certain U.S. Army activities, their general presence in municipal refuse, being listed as hazardous or toxic by RCRA, their representative nature with regard to various functional groups and a range of physical properties, and their amenability to available analytical methodologies.

Martenssen et al. (1999) investigated the effect of humic substances on the mobility of toxic metals in a mature landfill. Aeration increased the cation-exchange capacity, but decreased the buffering capacity and the metal-binding capacity. Leachates from the aerated landfill contained less than half the amount of aluminum, iron and molybdenum and more than double the amount of calcium, magnesium, sulfur and zinc of the leachates derived from an identical, but anaerobic, landfill. The leachate from the original landfill treated with leachate from the aerated landfill contained more than twice as much aluminium, boron, cadmium, chromium, copper, iron, lead, magnesium, nickel, phosphorus, potassium, sulfur and zinc than leachate from the identical anaerobic landfill. It was concluded that the mobility of deposited metals in landfills will change over time as the ageing of the landfills progresses and conditions become more oxidized.

San and Onay (2001) studied the impacted of various leachate recirculation regimes on municipal solid waste degradation, two landfill-simulating reactors, one with leachate recycle and one without, were constructed and placed at a constant room temperature (34°C). Both reactors were filled with a municipal solid waste mixture representing the typical solid waste composition with the initial amount of waste was 13 kg. Leachate recirculation volume and frequency were changed periodically. The results showed that increased frequency of leachate recirculation accelerates the stabilization rate of waste matrix. About 2 L of recirculated leachate and four times per week recirculation strategy were found to provide the highest degree of waste stabilization. Additionally, the results confirmed that leachate recirculation is a very feasible way for in situ leachate treatment.

Onay and Pohland (2001) found attenuation of nitrogen and sulfate in simulated landfill bioreactors. The characteristics of leachate from landfills vary according to site-specific conditions. Leachates from old landfill are often rich in ammonia nitrogen, posing potential adverse environmental impacts in the case of uncontrolled discharge. At landfills where leachate recirculation is practiced, leachate ammonia concentrations may accumulate to higher levels than during the single pass leaching. Using leachate recirculation with system modifications, separate aerobic and anoxic zones for nitrification and both autotrophic and heterotrophic denitrification can be provided. Results from simulated landfill bioreactors indicated that both nitrogenous and sulfur compounds can be attenuated through autotrophic denitrification, and leachate nitrate concentrations of 750 mg/L reduced to less than 1 mg/L by denitrification to nitrogen gas promoting this very common process in a landfill environment results in the reduction of both leachate ammonia and sulfate concentrations.

Turajane (2001) evidenced solid waste degradation behavior and comparison of methane production efficiency from high solid anaerobic digestion with and without leachate recycle was performed. There were different recycle ratio of 10, 25, and 50 percent applied in this study. The result in this study showed that increasing the recycle rations from 10, 25, and 50 percent resulted in rising biogas production of 25.74, 156.2, and 129.14 litters, respectively. And percent methane content in off-gas to 40.88, 48.61, and 52.45 percent, respectively. Therefore, a leachate recycle system was found beneficial and enhanced a more complete conversion of organic waste to methane than a system with no recycle of leachate.

Erses and Onay (2003) studied the in-situ heavy metal attenuation in landfills under methanogenic conditions. Two landfill simulating reactors, one with leachate recirculation and the other without, were operated in a constant room temperature at 32 ° C. these reactors were filled with shredded and compacted municipal solid waste having a typical solid waste composition of Istanbul region. After the onset of the methanogenic conditions, the selected heavy metals including iron, copper, nickel, cadmium and zinc were added according to amounts suggested for codisposal. The results of the experiments indicated that about 90% of all heavy metals were precipitated from the reactors within the first 10 days due to the establishment of highly reducing environment and the formation of sulfide from sulfate reduction, which provided heavy metal precipitation.