DOKUZ EYLÜL UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

THE EFFECT OF HEAVY METAL CONCENTRATIONS IN SOLID WASTE ON METHANE PRODUCTION IN LANDFILL AREAS

by
Turgay ODABAŞ

October, 2007
İZMİR

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We have read the thesis entitled "**THE EFFECT OF HEAVY METAL CONCENTRATIONS IN SOLID WASTE ON METHANE PRODUCTION IN LANDFILL AREAS"** completed by **TURGAY ODABAŞ** under supervision of **ASSIST. PROF. DR. GÖRKEM AKINCI** and we certify that in our opinion it is fully adequate, in scope and in quality, as a thesis for the degree of Master of Science.

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TURGAY ODABAŞ

THE EFFECT OF HEAVY METAL CONCENTRATIONS IN SOLID WASTE ON METHANE PRODUCTION IN LANDFILLS AREAS

ABSTRACT

The effect of heavy metals presence in waste body on the methane production in landfill areas is studied here. Three different waste mix containing different amounts of heavy metals are used in the reactors and the systems are operated for 15 weeks. Total gas and methane production in the systems are followed, leachate properties are determined and heavy metal levels and bounding forms are analyzed during the study.

It is found that dissolvable heavy metals are negatively effecting the gas and methane production in landfill areas. Form distributions of heavy metals may change during anaerobic decomposition. Acidic conditions caused by the heavy metals are related with their dissolvable portions. Leachate from the areas with high heavy metal content has higher heavy metal content and hart to be treated.

Keywords: methane, landfill, heavy metals,

ÇÖP DEPOLAMA ALANLARINDAN METAN GAZI ÜRETİMİNE KATI ATIKLARDAKİ AĞIR METAL KONSANTRASYONLARININ ETKİSİ

ÖZ

Çalışma kapsamında atık bünyesinde bulunan ağır metallerin toplam gaz ve metal üretimine etkisi araştırılmıştır. Farklı ağır metal konsantrasyonundaki üç atık ile 15 hafta süresince anaerobik reaktörde çalışılmıştır. Reaktörlerde oluşan toplam gaz ve metal içeriği, sızıntı suyu özellikleri ve ağır metallerin miktarları ile form dağılımları incelenmiştir.

Sonuç olarak, ağır metallerin çözünebilir formlarının depolama alanındaki varlığının toplam gaz ve metal oluşumunu negatif yönce etkilediği, anaerobik parçalanma sırasında ağır metallerin formlarının değişebildiği, sızıntı suyunun ağır metal içeriği fazla olan depolama alanlarında daha kirli olduğu ve arıtılmasında güçlükler yaşanacağı belirlenmiştir.

Anahtar Kelimeler: metan, deponi, ağır metaller

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CHAPTER ONE
AIM AND CONTENT OF THE STUDY

Heavy metals exist in both industrial and domestic solid wastes. Domestic wastes include heavy metals such as Pb, Ni, Hg, Cu and Cd. Accumulated heavy metal content in sanitary landfill bodies can be decreased if the wastes are collected separately.

Fundamentally, wastes are classified as hazardous according to their heavy metal content. Hazardous wastes should be collected, transported, and disposed of separately and individually. But in some areas industrial wastes and domestic wastes are collected together and they are stored in the same landfill area together.

There are two major goals of this study as follows;

First is observing the effect of heavy metal concentrations in solid waste on the methane production in domestic solid waste landfill areas.

And the second one is searching the possibilities of disposing the heavy metal containing industrial solid wastes in domestic solid waste landfill areas.

To realize the aims of this study first a literature survey is completed to gather the information about waste properties, disposal methods, landfilling, the biochemical activities taking place in landfill bodies, landfill gas and methane production stages, factor effecting the gas production in landfills, and properties and effects of heavy metals mostly seen in solid waste.

In the second part of the study anaerobic reactor systems are used to observe the methane production from the solid waste that contains different levels of heavy metal concentrations. The levels of heavy metals in solid waste are determined according to the Hazardous Waste Control Regulation of Turkish Republic. Three different initial

heavy metal concentrations are studied to obtain a concentration spectrum from “inert” to “hazardous”. The studied heavy metals are Ni, Cu, Pb, and Zn.

The heavy metals in the waste are determined by using Total Acid Digestion of EPA and the concentrations are determined by using ICP-OES. The initial forms of heavy metals in wastes studied are also determined by using Tessier Sequential Extraction Method followed by ICP-OES.

The systems are operated for 15 weeks and leachate properties are determined after the reactors are emptied. Gas and methane measurements are followed during the operation interval to detect the effect of heavy metal presence in waste on methane production.

CHAPTER TWO
HISTORICAL

2.1 Sources and Types of Solid Wastes

The term of solid wastes is all – inclusive and encompasses all sources, types of classifications, compositions and properties. Knowledge of the sources and types of solid wastes along with data on the composition and rates of generations is basic to design and operation of the functional elements associated with the management of solid wastes. As a basis for subsequent discussions, it will be helpful to define the various types of solid wastes. Three categories are considered in general:

- Municipal solid wastes
- Industrial solid wastes
- Hazardous solid wastes

2.1.1 Municipal Solid Wastes (MSW)

Any garbage, refuse, sludge from a waste treatment plant, water supply treatment plant, or air pollution control facility and other discarded material, including solid, liquid, semi-solid material resulting from industrial, commercial, mining, and agricultural operation, and from community activities are defined as municipal solid wastes (Kınay, 2003).

Generally, the composition of MSW is dependent on consumer habits in the region, the waste management legislation in force, and the extent to which source-segregation is practiced as well as the composition of the materials that end up as waste (Tunç, 2005).

Municipal solid wastes consist of food wastes, rubbish, ashes and residues, demolition and construction wastes, special wastes and treatment plant wastes. Food wastes that are the animal, fruit or vegetable residues (also called garbage) resulting from the handling, preparation, cooking and eating of foods. They are putrescible

(biodegradable), so they will decompose rapidly, especially in warm weather (Kınay, 2003).

Table 2.1 General Sources of Municipal Solid Wastes

Source	Typical Facilities in the Source	Solid Waste Type
Residential	Single – family and multifamily dwelligs, low - medium - and high – rise apartments, etc.	Food wastes, rubbish, ash, special wastes
Commercial	Stores, restaurants, markets, office buildings, hotels, motels, print shops, auto repair shops, medical facilities and institutions, etc.	Food wastes, rubbish, ashes, demolition and construction wastes, special wastes, occasionally hazardous wastes
Open areas	Streets, alleys, parks, vacant lots, playgrounds, beaches, highways, recreational areas, etc.	Special wastes, rubbish
Treatment plant sites	Water, wastewater and industrial treatment processes, etc.	Treatment plant wastes, principally composed of residual sludge.

Rubbish are combustible (paper, cardboard, plastics, textiles, rubber, leather, wood, furniture and garden trimmings) and noncombustible (glass, crockery, tin cans, aluminum cans, ferrous and nonferrous metals, dirt and construction wastes) solid wastes, excluding food wastes or other putrescible materials (Kınay, 2003).

Higher incomes and economic growth also tend to have an impact on the composition of wastes. Wealthier individuals consume more packaged products, which results in a higher percentage of inorganic materials – metals, plastics, glass, textiles, and so on – in the waste stream. Higher volumes of wastes and a changing composition have a profound impact on waste management practices (Tunç, 2005).

2.1.1.1 Biowastes

The last decade has seen a significant increase in the volume of biowaste diverted from landfill and turned into humus rich compost, closing the recycling loop. Biowaste refers to any organic waste that is capable of undergoing anaerobic or aerobic decomposition and includes the following (Tunç, 2005):

- ✓ Food waste
- ✓ Garden waste
- ✓ Kitchen waste
- ✓ Bio solids (sewage sludge)
- ✓ Manure
- ✓ Sawdust

Municipalities' receiving solid waste services, 25.014million tones of yearly average of solid waste were collected from 3.028 municipalities in 2004 (State Institute of Statistics, 2004). From these results daily amount of solid waste is calculated as 1.30 kg/capita/day in summer, 1.29 kg/capita-day in winter and 1.31 kg/capita-day for yearly average (Tunç, 2005).

2.1.2 Industrial Wastes

All solid, liquid, and gaseous waste resulting from the manufacture of goods are defined as industrial waste. Industrial wastes are those wastes arising from industrial activities and typically include rubbish, ashes, demolition and construction wastes, special wastes and hazardous wastes.

The composition of industrial waste depends on the kind of industries involved. Basically, industrial waste includes components similar to domestic and commercial source waste, including food wastes from kitchens and canteens, packaging materials, plastics, paper and metal items. Some production processes, however, utilize or generate hazardous (chemical or infectious) substances. Disposal routes for

hazardous wastes are usually different from those for non – hazardous waste and depend upon the composition of the actual waste type (Kınay, 2003).

2.1.3 Hazardous Wastes

Hazardous wastes are defined as wastes or combinations of wastes that pose a substantial present or potential hazard to humans or other living organisms because;

- Such wastes are non-degradable or persistent in nature,
- They can be biologically magnified
- They can be lethal
- They may otherwise causes to tend to cause detrimental cumulative effects.

In the past, hazardous wastes were often grouped into the following categories:

(1) Radioactive substances, (2) chemicals, (3) biological wastes, (4) flammable wastes and (5) explosives. The chemical category includes wastes that are corrosive, reactive or toxic whereas hazardous biological wastes contain such wastes from hospitals and biological research facilities.

Hazardous wastes are generated in limited amounts throughout most industrial activities. In terms of generation, the concern is with the identification of the amounts and types of hazardous waste developed at each source, with emphasis on those sources where significant waste quantities are generated.

In Turkey, the amount of solid waste collected by municipalities is increased from 17 million tones to 25 million tones between the years of 1994 and 2004. According to results of an extensive research conducted by State Institute of Statistics (SIS) in 2004, the daily amount of municipal solid waste collected by 3028 municipalities is 68.534 tons. Approximately 77 percent of the garbage was disposed of in the main city dumping sites (i.e. open dumps), which are either operated by municipalities (public) or by private establishments, while only 27 percent of municipal solid waste was disposed in the sanitary landfills (Kınay, 2003).

Waste generation rates are affected by socioeconomic development, degree of industrialization, and climate. Generally, the greater the economic prosperity and the higher percentage of urban population, the greater the amount of solid waste produced (Urban Development Sector Unit East Asia and Pacific Region, 1999).

2.2 Industrial Wastes Containing Heavy Metals

The content of heavy metals in waste is primarily a consequence of the intended use of heavy metals in industrial products. At the end of their useful life all products will end up in waste to the extent they are not attractive for recycling. Heavy metals may, however, also be lost to waste during production and use phases. Losses in the manufacturing process are often disposed of as manufacturing waste, while products may be exposed to wear and tear inclusive corrosion during the use phase. Identification of the actual sources for heavy metals observed in different waste types and waste products may only be done with some uncertainty. Lead atom in flue gas cannot tell whether it originates from lead pigments in plastic or a lead battery been disposed of as combustible waste. A useful tool in this context is Substance Flow Analysis, which based on a knowledge on applications for the substance in question and flow patterns for relevant products allows for the development of a realistic picture of significant sources for different waste types. The analysis of sources to waste has focused on solid waste (European Commission, 2002).

2.2.1 Lead

It is characteristic for lead, that many different products containing lead will end up in waste management systems and be a source of lead to incineration plants and/or landfills. Important sources include: Plastics, fishing tools, lead crystal glass inclusive cathode ray tubes, ceramics, solders, pieces of lead flashing and many other minor products. To these waste types must be added residues from metal shredding, steel reclamation and cable reclamation.

Table 2.2 Applications of lead and disposal pathways for lead products

Product group	Comment	Disposal or recovery of discarded products			Emitted or lost directly to the environment
		MSWI or sanitary landfills	Recovery	Chemical waste disposal	
Metallic uses					
Batteries	Lead content of lead batteries is app. 55-60%	+	+++		
Cables sheeting	Today mostly used for cables in the ground or undersea, Significant amount of lead sheeted cables used both in the ground and in-door are still in service	+	++		+++ Left in the ground or sea-floor
Sheets for buildings	Lead sheets are used in building and construction industry mainly for flashing and weathering protection.	+	+++		+ Corrosion
Sheets for chemical industry	Lead sheet can be used for watertight linings for tanks and vessels		+++		
Leaded window frames	Extruded lead frames holding stained glass Also available as self-adhesive extruded lead tape	+++	+		
Solders for electronics	Solders for electronic typically contain 40 % lead, alloyed with tin	++	++ EEE waste		
Solders for other applications	Solders are used for many applications: plumbing, light bulbs, cans, etc. The lead content vary from 35% to 99%	++ Solders for light bulbs, cans etc.	+ With zinc and other metals. Recycled from filter dust		
Ammunition	Lead is used in shots, bullets and other types of ammunition	+ Shot in game. Shot and bullets used on shooting ranges	+ Shot and bullets used on shooting ranges		+++
Fittings, bearings etc. of lead alloys	Lead is used in brass, steel and aluminium to improve the machineability of the materials. Brass used for fittings, taps etc. contains typically 2-3% lead. Bronze for bearings often contain between 5 and 20% lead	+ Small parts + Slag from recycling processes	+++	+ Dust from manufacturing processes	
Zinc coating (hot galvanisation)	Zinc coating may contain a few percent lead.	+	+++ Recycled from filter dust		
Weights for fishing tools and anchors	Lead weights are used for small sinkers by angles and for weights on fishing nets used for professional fishing	++	++		++
Balance weights for vehicles Plating of gasoline tanks	Lead weights for balancing of wheels	+	+++		+
Keels	Lead is used in keels for yachts		+++		

Table 2.2 Applications of lead and disposal pathways for lead products (continue)

Product group	Comment	Disposal or recovery of discarded products			Emitted or lost directly to the environment
		MSWI or sanitary landfills	Recovery	Chemical waste disposal	
Lead tubes for drain and water pipes Lead joints for pipes	Lead is hardly used for lead pipes today, but significant amount of lead pipe work are still in service	+	++		
Radiation shielding	Used both in protective walls, aprons and foils for X-ray films	+ Aprons and foils	+++		
Other: Toys, curtains, candlesticks, foils, organ pipes etc.	Tin-lead alloys (pewter) containing 5-50% lead are used for miniatures (toy), candlesticks, tableware, organ pipes etc. Lead strings are used for curtains. Lead foil is used for decorative means,	+++	+ Relevant for organ pipes		
Uses as chemicallmineral					
Gasoline additives	Lead in gasoline additives is nearly 100% phased out in the EU				+++
PVC stabiliser	About 0.7-2% Pb as stabiliser in many types of rigid PVC for out-door use	+++	+		
Pigments in plastic	Lead chromate for yellow and red colours contains 64% lead	+++			
Pigments in paint and ceramics	Lead chromate for yellow and red colours contains 64% lead Lead carbonate previously used for white colours	+++		+	
Siccative in paint	Lead naphthenate in concentrations of 0.5-2% used as siccative in alkyd-paint	+++			
Rust-inhibitive primers; miniate	Red lead (Pb_3O_4) used in some rust-inhibitive primers used e.g. for maintenance of old iron-constructions	+ Slag from steel reclamation	+++ Recycled from filter dust from steel reclamation	+	+
Lubricants	Lead naphthenate may be used as a lubricant	?			
Cathode ray tubes	The neck and funnel of cathode ray tubes contains about 25% lead whereas the faceplate contains 2-3% lead in the form of lead silicates	++	++ EEE waste		
Other applications of lead crystal glass	Crystal glass contains 24-36% lead oxide, PbO, semicrystal glass contains 14-24% PbO Lead silicate glass is used in fluorescent tubes and light bulbs	+++			
Glazing	Lead silicate ($PbSiO_3$) used for glazing in tableware and	+++			

Note: The number of + indicates the disposal pattern within each product group and does not give any indication of quantities among the groups.

* Only application where a substantially part of the products is emitted is indicated.

2.2.2 Mercury

Important sources for mercury to waste include: Dental amalgam, measurement and control devices inclusive thermometers, batteries, tubes and lamps etc. It is interesting to note the significant differences between countries, which may be explained by differences in regulation as well as tradition (European Commission, 2002).

Table 2.3 Applications of mercury and disposal pathways for mercury products

Product group	Comment	Disposal or recovery of discarded products			Emitted or lost directly to the environment *
		MSWI or sanitary land-fills	Recovery	Chemical waste disposal	
Manometers, relays, measuring devices and control equip-ment	Mercury used as conductive or ex-panding liquid Electrochemical properties used in i.a. calomel electrodes	++	++	+	
Gold mining	Gold can be dissolved in mercury Not relevant in EU Member states				+++
Use as chemi-cal/vapour					
Batteries, button cells	The mercury content of mercury oxide button cells is about 30% whereas silver oxide cells may contain up to 1% mercury	++	+	++	
Other batteries	Alkaline batteries have formerly con-tained mercury, but alkaline batteries are today "mercury free" in OECD countries	+++		+	
Paints	Mercury has formerly been used as pigment in paint, The use today in the EU is assumed to be insignificant	+++			
Fluorescent tubes and bulbs High-voltage dis-charge lamps	Mercury vapour emits light when charged	++	+	+	+ When tubes or lamps are bro-ken
Laboratory chemi-cals	A number of compounds, e.g. mercury sulphate, mercury oxide, mercury nitrate are used as laboratory chemical			+++	
Pesticides and bio-cides	Formerly widely used as biocide and pesticide. The use today in the EU is assumed to be insignificant				+++

Table 2.3 Applications of mercury and disposal pathways for mercury products (continue)

Product group	Comment	Disposal or recovery of discarded products			Emitted or lost directly to the environment *
		MSWI or sanitary land-fills	Recovery	Chemical waste disposal	
Metallic uses					
Chlor-alkali industry	Mercury used as electrode in the pro-duction of chlorine and alkali		+	+	
Dental amalgams	Mercury accounts for 44-51% by weight of dental amalgams	++ Lost teeth	++ Dental waste	+ Dental waste and lost teeth	++ By burial or cremation
Thermometers	Mercury used as expanding liquid	+++		+	+
Tilt switches and wiring devices	Mercury used as conductive liquid in tilt switches of water pumps, cars, flashlight, etc.	++ residues from recycling ac-tivities	+	+	

Note: the number of + indicates the disposal pattern within each product group and does not give any indication of quantities among the groups
* Only applications where a substantially part of the products is emitted is indicated.

Consumption of the different kinds of batteries has increased, but the Hg content has decreased. Nowadays, in general, alkaline-manganese batteries contain 0.025 wt. % Hg, while manganese oxide batteries do not contain any added Hg. The use of Hg lamps in society is increasing, but Hg amount in individual lamps has decreased. Energy costs and saving campaigns motivate people to use energy saving types of lamps.

There is wide range of waste treatment methods which are generally based on thermal, physical, chemical or biological processes. The disposal methods for waste are generally: (a) landfills; (b) incineration; (c) composting; (d) recycling/recovery. Hg containing waste is not however, suitable for landfills, composting, and requires special treatment when incinerated (Mukherjee, Zevenhoven, Brodersen, Hylander & Bhattacharya, 2004).

2.2.3 Cadmium

For cadmium the picture is somewhat simpler, as the use of cadmium has been restricted for some years and Ni-Cd batteries today is the all-dominating product. However, to understand the picture of sources to incineration plants, it is necessary to

remember uses as pigments and stabilizers in plastic as well as plating on steel, which have been significant uses 1-2 decades ago. Many of the relevant cadmium products were quality goods with an expected lifetime of 10- 20 years or even more (e.g. PVC-window frames). Such goods are only slowly released to waste. Concerning landfills table 3 indicates that manufacturing waste is a source of the same magnitude as industrial products in municipal waste (European Commission, 2002).

Table 2.4 Application of cadmium and disposal pathways for cadmium products

Product group	Comment	Disposal or recovery of discarded products			Emitted or lost directly to the environment *
		MSWI or sanitary land-fills	Recovery	Chemical waste disposal	
Metallic uses					
Plating and coating	Plating and coating on iron, steel, aluminium and brass Used mainly in electrical, electronic automobile and aerospace industry	+++ Residues from metal recla-mation	+ With metals Recycled from filter dust		
Silver-cadmium alloys	Silver jewellery often contains small amount of cadmium. Some silver jew-ellery may contain up to 30% Cd.	++	++		
Copper-cadmium alloys, solders and other alloys	Copper with 0.6-1.2% cadmium used for wires for railway traction Cd containing solders are used for soldering aluminium (40% Cd in sol-der) and steel Cadmium is used on some bearing alloys and fusible alloys	+ Minor parts + Residues from metal recla-mation	+ With metals Recycled from filter dust		
Use as chemi-cal/mineral					
Ni-Cd batteries	Sealed cells (closed batteries) are used for electronics and vehicles Vented cells (open batteries) are mainly used for power backup	++	++	+	
PVC stabiliser	About 0.7-2% Cd as stabiliser in many types of rigid PVC for out-door use	+++	+		
Pigments	Pigments are used in plastic (main use), ceramics, glass and paint	+++	+ Transport		
Photovoltaic cells	Cadmium telluride and cadmium sul-fide are used in some types of photo-voltaic cells	?			

Note: The number of + indicates the disposal pattern within each product group and does not give any indication of quantities among the groups.
• Only application where a substantially part of the products is emitted is indicated.

2.2.4 Chromium

The environmental concerns related to chromium are focused on applications like tanning, wood preservation and pigments and dyes for plastics, paint and textiles. Chromium alloys and in particular stainless steel are by far the dominating field of application for chromium, but normally not regarded as a serious waste problem due to the high value of chromium alloys, which motivates collection for recycling. One may, however, pay attention to that many types of stainless steel are not magnetic and cannot be separated from waste streams by magnetic separation.

Sanitary landfill is the most, Commercial and industrial wastes, which may contain hazardous substances, such as heavy metals, organic solvents, radioactive wastes etc. are also received by landfills in many countries. Batteries, paints, dyes and inks in paper, pesticides and fertilizers in yard waste are examples of household and commercial wastes, which contain high quantities of heavy metals. Incineration ash is another type of waste that is disposed to landfills. High amounts of heavy metals are present in this and could severely affect the overall processes occurring in a landfill environment.

The major sources of heavy metals in landfills are the co-disposed industrial wastes, incinerator ashes, mine wastes and household hazardous substances such as batteries, paints, dyes, inks, etc. The most common heavy metals in landfills are iron, cadmium, copper, zinc and nickel (Erses, Fazal, Onay & Craig, 2005).

Table 2.5 Application of chromium and disposal pathways for chromium Products

Product group	Comment	Disposal or recovery of discarded products			Emitted or lost directly to the environment *
		MSWI or sanitary land-fills	Recovery	Chemical waste disposal	
Metallic uses					
Stainless steel	Average Cr content of stainless steel is about 17%	+ Kitchen ware and other small items	+++		
Other alloys	Chromium is used in a variety of alloys - often at a content of less than 1%	+ small items	+++		
Plating	Chromium is used in layers of approximately 0.2-1.2 µm for decorative coating on steel, coppers alloys and plastics Chromium is used in layers of 2.5-500 µm for hard chromium plating of steel Chromium compounds are used for the plating, but the finished products contain chromium as metal	+ Peels, dust, plastics + May end up in filter dust and slag from secondary metal production	+		
Use as chemicalmineral					
Colours and pigments	Various chromium compounds used - both Cr(III) and Cr(VI) Used for plastics, ceramics, corrosion inhibition	+++		+	
Textile dyes	Various chromium compounds used - both Cr(III) and Cr(VI)	+++		+	
Leather tanning	Various chromium compounds used - both Cr(III) and Cr(VI)	+++		+	
Wood preservatives	Cr(VI) is used for preservatives	++		(+)	+
Metal surface treatment	Chemicals do not end in the finished products			+	
Refractories	Lining furnaces and kilns for production of copper, nickel, cement and glass	+++			
Laboratory chemicals	Many different chemicals			++	
Catalysts	Are typically returned to the manufacturer for regeneration and from here to recovery.		+		

Note: The number of + indicates the disposal pattern within each product group and does not give any indication of quantities among the groups.
*Only application where a substantially part of the products is emitted is indicated.

2.3 Solid Waste Disposal Methods

2.3.1 Introduction

Solid Waste Disposal, disposal of normally solid or semisolid materials, resulting from human and animal activities that are useless, unwanted, or hazardous. Solid wastes typically may be classified as follows (n.d.):

Garbage: decomposable wastes from food

Rubbish: non-decomposable wastes, either combustible (such as paper, wood, and cloth) or noncombustible (such as metal, glass, and ceramics)

Ashes: residues of the combustion of solid fuels

Large wastes: demolition and construction debris and trees

Dead animals

Sewage-treatment solids: material retained on sewage-treatment screens, settled solids, and biomass sludge

Industrial wastes: such materials as chemicals, paints, and sand

Mining wastes: slag heaps and coal refuses piles

Agricultural wastes: farm animal manure and crop residues.

During the 1980s, solid waste management issues began to pose potential crises in many areas of the country because of increasing solid waste generation, shrinking landfill capacity, rising disposal costs, and strong opposition to new solid waste facility sitting.

EPA recommends an integrated, hierarchical approach to waste management using four components: source reduction, recycling, combustion, and landfilling. This comprehensive approach addresses critical junctures in the manufacture, use, and disposal of products and materials to minimize wastefulness and maximize value. It favors source reduction to reduce the volume and toxicity of waste and to increase the useful life of products. Recycling, including composting is the preferred waste management approach to divert waste from landfills and combustors.

Combustion is used to reduce the volume of waste being disposed and to recover energy from this process, and landfilling is used for final disposal of non-recyclable and non-combustible material. The goal of this approach is to use a combination of all of these methods (shown in Figure 2) to safely and effectively handle the municipal solid waste stream with the least adverse impact on human health and the environment. Each community should choose a mix of alternatives that most effectively meets its needs. The four elements of the hierarchy are discussed below (Resource Conservation and Recovery Act, [RCRA], 2001).

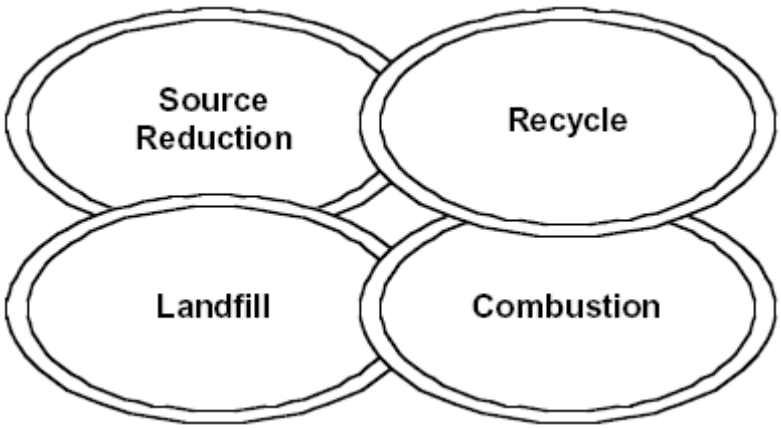


Figure 2.1 Hierarchy of integrated waste management.

2.3.2 Source Reduction

Source reduction programs seek to change people's behavior by helping them find less waste intensive practices or alternative uses for existing waste materials without having to dispose of or recycle them. Essentially, source reduction eliminates the need to manage waste. EPA considers source reduction to include reuse activities. Reusing materials in their current form, without any conversion process or transportation, reduces the need for manufacturing new products, thereby saving valuable resources and creating less waste for disposal.

Source reduction is a front-end approach to addressing MSW problems by changing the way products are made and used. Focusing on source reduction is an attempt to move away from the traditional "end-of-the-pipe" waste management

approach used in the past. Source reduction is defined as the design, manufacture, and use of products in a way that reduces the quantity and toxicity of waste produced when the products reach the end of their useful lives. Source reduction activities fall into some basic categories:

• Product reuse (e.g., reusable shopping bags and coffee mugs)
• Reduced material volume (e.g., less unnecessary packaging for products)
• Reduced toxicity of products (e.g., use substitutes for lead, cadmium, mercury, and other toxics)
• Increased product lifetime (e.g., design products with longer useful life)
• Decreased consumption (e.g., changing consumer buying practices, bulk purchasing).

Businesses, households, and state and local governments can all play an active role in implementing successful source reduction programs. Businesses can implement source reduction through the design and manufacture of products that use less packaging or that use substitutes for toxic constituents. Many businesses have also used source reduction to significantly reduce the amount of material that enters the waste (e.g., reusing packaging for shipping products, double-sided copies, maintaining equipment to extend its useful life, reusable envelopes). These changes have often resulted in significant savings in waste management costs and raw material purchasing. If source reduction is going to play a key role in overall waste reduction, consumers also must incorporate this concept into their buying practices. Consumers purchasing products that reduce unnecessary packaging or that eliminate toxic constituents will increase demand for products with these attributes. Finally, source reduction must be part of state and local governments' strategic long-term planning to address solid waste problems. Some states have passed legislation to reduce lead, cadmium, chromium, and mercury in packaging. Some local governments have established model communities that use source reduction and recycling concepts as the focus of their strategic waste management plans (RCRA, 2001).

2.3.3 Recycling

Municipal solid waste recycling refers to the separation and collection of wastes and their subsequent transformation or remanufacture into usable or marketable materials. Recycling, including composting, diverts potentially large volumes of material from landfills and combustors, and stops unnecessary waste of natural resources and raw materials. Recycling collection and separation programs vary in degree of implementation: some may be simple drop-off programs, while others may involve comprehensive curbside collection and complex source separation at a material recovery facility. Successful recycling, however, is more than the separation and collection of post consumer materials. These are only the first steps post consumer materials must also be reprocessed or remanufactured, and only when the materials are reused is the recycling loop complete. Centralized composting of yard and food wastes is also classified as recycling. Some communities have begun to conduct large-scale centralized composting of yard waste in an effort to save landfill capacity. Individuals are also helping to reduce waste by composting yard waste in their backyards, and by not bagging grass clippings or other yard wastes (these activities are actually classified as source reduction). Composting yard waste has seen tremendous growth in the past eight years (RCRA, 2001).

2.3.4 Combustion

For centuries, burning has been a popular method of reducing the volume and the odor of garbage. Until the early 1970s, Americans routinely managed much of their trash by burning it. People often burned large-volume combustible trash such as leaves in their backyards, while dump operators purposely set fires in waste pits to reduce volume. As concern about air pollution increased, local governments began to impose restrictions on uncontrolled burning of trash. The Clean Air Act of 1970 essentially banned uncontrolled burning of solid waste. The energy crisis of the 1970s also influenced changes in the handling of MSW. A more sophisticated system of incineration was developed that could use waste as a fuel to produce energy. Modern combustion facilities no longer just destroy garbage, but instead are

designed to recover energy that is used to produce steam and electricity. These waste-to-energy facilities can be used in conjunction with source reduction and recycling programs, because many items those are traditionally recycled, such as aluminum cans and glass, have low heating values.

Waste-to-energy units and incinerators are not really waste disposal facilities, but waste reduction units. After incineration, the noncombustible component of MSW remains as ash. Two types of ash are generated during incineration: fly ash, which collects in the air pollution control devices which "clean" the gases produced during the combustion of the waste; and bottom ash, which collects on the bottom of the combustion unit and comprises approximately 75 to 80 percent of the total ash. EPA studies indicate that fly ash generally contains the highest concentration of inorganic chemical constituents. Municipal waste combustion ash is periodically removed from the incinerator and usually land disposed, either in a MSW landfill or a "monofill" specifically intended for the ash. This procedure presents potential threats to human health and the environment due to the risks of inhalation near combustion and disposal sites (RCRA, 2001).

Municipal solid waste (MSW) incineration plants tend to be among the most expensive solid waste management options, and they require highly skilled personnel and careful maintenance. For these reasons, incineration tends to be a good choice only when other, simpler, and less expensive choices are not available. Because MSW plants are capital-intensive and require high maintenance costs and comparatively higher technically trained operators, they are commonly adopted by developed countries. However, high capital and maintenance costs may make MSW incineration beyond the reach of many of the lesser developing countries (n.d.).

2.3.4.1 Incineration Advantages

Incineration is an efficient way to reduce the waste volume and demand for landfill space. Incineration plants can be located close to the center of gravity of waste generation, thus reducing the cost of waste transportation. Using the ash from

MSW incinerators for environmentally appropriate construction not only provides a low cost aggregate but further reduces the need for landfill capacity. In particular, incineration of waste containing heavy metals and so on should be avoided to maintain a suitable slag quality. Energy can be recovered for heat or power consumption. All waste disposal alternatives eventually decompose organic materials into simpler carbon molecules such as CO2 (carbon dioxide) and CH4 (methane). The balance between these two gases and time frame for the reactions varies by alternative. Incineration provides the best way to eliminate methane gas emissions from waste management processes. Furthermore, energy from waste projects provides a substitute for fossil fuel combustion. These are two ways incineration helps reduce greenhouse gas emissions. One of the most attractive features of the incineration process is that it can be used to reduce the original volume of combustibles by 80 to 95 percent. Air pollution control remains a major problem in the implementation of incineration of solid waste disposal. In the United States, the cost of best available technology for the incineration facility may be as high as 35 percent of the project cost. The cost of control equipment will, however, depend upon the air pollution regulations existing in a given lesser developing country. Waste incineration may be advantageous when a landfill cannot be sited because of a lack of suitable sites or long haulage distances, which result in high costs.

2.3.4.2 Incineration Disadvantages

An incineration plant involves heavy investments and high operating costs and requires both local and foreign currency throughout its operation. The resulting increase in waste treatment costs will motivate the waste generators to seek alternatives. Furthermore, waste incineration is only applicable if certain requirements are met. The composition of waste in developing countries is often questionable in terms of its suitability for auto combustion. The complexity of an incineration plant requires skilled staff. Plus, the residues from the flue gas cleaning can contaminate the environment if not handled appropriately, and must be disposed of in controlled and well-operated landfills to prevent ground and surface water pollution (n.d.).

2.3.5 Landfilling

Even with the use of source reduction, recycling, and combustion, there will always be waste that ultimately must be disposed. Many communities are having difficulties sitting new landfills largely because of increased citizen and local government concerns about the potential health risks and aesthetics of having a landfill in their neighborhoods. EPA promulgated new technical standards for MSW landfills in 1991. These new standards address location restrictions, design and operating criteria, groundwater monitoring, financial assurance, closure and post-closure requirements, and corrective action (RCRA, 2001).

Sanitary landfill is the most common method of disposal of solid waste all over the world and are the oldest and the most popular ultimate disposal option often enabling the reclamation of derelict land to be achieved. It also has the advantages of flexibility and reliability and it is quite easy to predict the future costs of direct landfill. As well as municipal solid waste, commercial and industrial wastes, which may contain hazardous substances, such as heavy metals, organic solvents, radioactive wastes etc. are also received by landfills in many countries. Batteries, paints, dyes and inks in paper, pesticides and fertilizers in yard waste are examples of household and commercial wastes, which contain high quantities of heavy metals. Incineration ash is another type of waste that is disposed to landfills (Erses, Fazal, Onay & Craig, 2005).

2.3.6 Composting

Composting is a managed system that uses microbial activity to degrade raw organic materials, such as yard trimmings, so that the end-product is relatively stable, reduced in quantity (when compared to the initial amount of waste), and free from offensive odors. Composting can be done on a large or small scale, with the management requirements and intensity increasing dramatically as system size increases. In its simplest form, compostable material is arranged in long rows

(windrows) and turned periodically to ensure good mixing (United States Environmental Protection Agency [US EPA], 1998).

Compost is organic material that can be used as a soil amendment or as a medium to grow plants. Mature compost is a stable material with content called humus that is dark brown or black and has a soil-like, earthy smell. It is created by: combining organic wastes (e.g., yard trimmings, food wastes, manures) in proper ratios into piles, rows, or vessels; adding bulking agents (e.g., wood chips) as necessary to accelerate the breakdown of organic materials; and allowing the finished material to fully stabilize and mature through a curing process (EPA, 1998).

Natural composting, or biological decomposition, began with the first plants on earth and has been going on ever since. As vegetation falls to the ground, it slowly decays, providing minerals and nutrients needed for plants, animals, and microorganisms. Mature compost, however, includes the production of high temperatures to destroy pathogens and weed seeds that natural decomposition does not destroy (EPA, 1998).

The compost option affords the many advantages of biological systems: lower equipment and operating costs; in harmony with the environment; and results in a useful product. On the other hand, composting is sometimes attributed with disadvantages often associated with biological systems -- namely, a slow reaction rate and some unpredictability. Regarding the attributed disadvantages, slow reaction rate may be justified, in that retention times are in terms of weeks and months. However, the attribution of unpredictability is not justified (United Nations Environment Programme [UNEP], 2005).

2.3.7 Resource Recovery

Numerous thermal processes, now in various stages of development, recover energy in one form or another from solid waste. These systems fall into two groups: combustion processes and pyrolysis processes. A number of companies burn in-plant

wastes in conventional incinerators to produce steam. A few municipalities produce steam in incinerators in which the walls of the combustion chamber are lined with boiler tubes; the water circulated through the tubes absorbs heat generated in the combustion chamber and produces steam.

Pyrolysis, also called destructive distillation, is the process of chemically decomposing solid wastes by heat in an oxygen-reduced atmosphere. These results in a gas stream containing primarily hydrogen, methane, carbon monoxide, carbon dioxide, and various other gases and inert ash, depending on the organic characteristics of the material being pyrolyzed (n.d.).

2.3.8 Pyrolysis

MSW pyrolysis and in particular gasification is obviously very attractive to reduce and avoid corrosion and emissions by retaining alkali and heavy metals (except mercury and cadmium), sulphur and chlorine within the process residues, prevent largely Polychlorinated dibenzo-p-dioxine/-furans (PCDD/Fs) formation and reduce thermal NOx formation due to lower temperatures and reducing conditions. Slagging gasification may additionally provide for destructing hazardous compounds and vitrification of various residues. However, Cl and S species such as HCl and H_2S may still occur in the fuel gas yielded. Advantageously, smaller fuel gas volumes require lower dimensioned gas cleanups saving investment costs while using oxygen raises these costs but also the fuel gas calorific value (CV) and prevents thermal NOx formation.

Recently, advanced thermal waste treatment technologies combining pyrolysis (themolysis), gasification and/ or incineration in an integrated or modular approach are growing from long lasting RTD (refuse-derived fuel) activities into demonstration and even commercialization. The majority of the technologies aim primarily on improving environmental compliance mainly by effectively destructing air pollutants and vitrification of the solid process residues partly with materials recovery using high combustion or gasification temperatures thus saving disposal

costs or raise additional revenue although largely at the expense of overall energy output (Malkow, 2003).

2.4 Landfilling and Methane Production on Landfill Areas

2.4.1 Landfilling

Left unmanaged and uncontrolled, solid wastes openly dumped on the land: 1) generate liquid and gaseous emissions (leachate and landfill gas) that can pollute the environment and 2) represent a breeding ground for disease-bearing animals and microorganisms. Other risks to the public health and safety and to the environment are also posed by the uncontrolled land disposal of solid wastes.

Sanitary landfilling, which is the controlled disposal of waste on the land, is well suited to developing countries as a means of managing the disposal of wastes because of the flexibility and relative simplicity of the technology. Sanitary landfilling controls the exposure of the environment and humans to the detrimental effects of solid wastes placed on the land. Through sanitary landfilling, disposal is accomplished in a way such that contact between wastes and the environment is significantly reduced, and wastes are concentrated in a well defined area. The result is good control of landfill gas and leachate, and limited access of vectors (e.g., rodents, flies, etc.) to the wastes (n.d.).

Landfill sitting requires detailed investigation. Factors that need to be addressed include:

- Site capacity;
- Hydrology;
- Local topography and soils;
- Adjacent land uses;
- Climate;
- Local flora and fauna; and
- Road access.

2.4.1.1 Site Capacity

If practicable, a site with capacity for use over several decades should be acquired. Failing this the site acquired should provide at least 10 years of use as this will at least help minimize costs for site establishment and closure, keep operations running smoothly and provide adequate time to acquire the next site.

2.4.1.2 Hydrology

The pollution of surface and groundwater resources by leachate is a principal concern in relation to landfill location. Sites that contain, are located in, or are within 100 meters of the following are normally unsuitable for landfill facilities:

• Water supply catchments or ground water recharge areas;
• Coastal or estuarine areas subject to tidal inundation or storm surge;
• Wetlands;
• Areas which may be seasonally inundated, or are likely to be flooded in a major rain event; and
• Water bodies, watercourses or open drains.

Depending on the circumstances, high water table conditions may also render a site unsuitable for use as a landfill facility.

2.4.1.3 Local Topography and Soils

Topography: Careful consideration should be given to landforms in the vicinity of the disposal site as they may influence:

• The type of disposal method that can be utilized;
• The suitability of the site for construction of service facilities;
• Surface water drainage management;
• Groundwater conditions;
• Soil erosion risk; access to the site;

• Ability to screen the site from view; and
• The impact of winds on the site.

Ideally the slope of the site should not be greater than 5% (1 vertical to 20 horizontal).

Soils: Sufficient soil should be available to provide adequate covering for wastes. Soil structure should be suitable for construction of landfill cells and drainage works, as well as for excavation of trenches. The soil should also be of sufficiently low permeability to significantly slow the passage of leachate from the site. Sites in clay-rich environments are preferable, due to the low permeability, good workability and superior leachate retaining characteristics of these soils.

2.4.1.4 Adjacent Land Uses

Care should be taken to ensure that the establishment of a landfill facility will not jeopardize any environmentally sensitive areas or have a negative impact on existing or future land uses. Long term planning projections will be of help in assessing this. Risks to public health and impacts on the areas surrounding the landfill can be limited by providing buffer zones between the landfill and sensitive areas. Some appropriate buffer distances between the facility and other land uses are:

• Public roads > 100 meters
• Industrial developments > 200 meters
• Urban residential/commercial area > 500 meters; and
• Rural residential area > 1000 meters.

2.4.1.5 Climate

Consideration should be given to the local climatic conditions when sitting a waste disposal facility. For example: in the heavy rainfall situations which can occur in the Territory even sites with minimal slopes can incur severe erosion (through

sheet flow runoff) if extra care isn't taken with the drainage works; and, sites that are not protected from prevailing winds will require extra efforts to control litter and dust.

2.4.1.6 Local Flora and Fauna

Sites that contain protected or endangered fauna and/or flora, or sensitive ecosystems are unsuitable for landfill facilities. Possible impacts on ecosystems, flora and fauna include the contamination of sensitive wetland areas by leachate. Conversely, landfills often attract large numbers of birds, which can increase the risk to public health by spreading scavenged items away from the facility.

2.4.1.7 Road access

A landfill facility must have all weather access. Access roads should be located to minimize erosion and the alteration of drainage systems. Also, where possible the access road should be located so as to help keep the landfill screened from the main road past the facility. Access roads to the landfill should be designed and constructed to minimize costs and yet provide reasonably easy access for the expected traffic under the various conditions affecting the site (EPA, 2003).

2.4.1.8 Landfill Design

The particulars of the site chosen for the landfill and the needs and requirements of the communities it will serve will have to be taken into account when designing the facility. Some of the more important matters to be addressed include:

- The most appropriate type of landfill facility;
- The waste containment cell
- Water management;
- Site fencing and screening;
- Informative signs;

- Recycling and reuse;
- Staff facilities; and
- Vehicle wash areas.

2.4.1.9 Biological

The importance of biological reactions in a fill is due to the following two results of the reactions:

1. The organic fraction is rendered biologically stable and, as such, no longer constitutes a potential source of nuisances.
2. The conversion of a sizeable portion of the carbonaceous and proteinaceous materials into gas substantially reduces the mass and volume of the organic fraction.

At this point, it should be remembered that a fraction of the nutrient elements in the waste is transformed into microbial protoplasm. Eventually, this protoplasm will be subject to decomposition and, hence, it makes up a reservoir for breakdown in the future.

The wide varieties of fill components that can be broken down biologically constitute the biodegradable organic fraction of MSW. This fraction includes the garbage fraction, paper and paper products, and "natural fibres" (fibrous material of plant or animal origin). Biological decomposition may take place either aerobically or an aerobically. Both modes come into play sequentially in a typical fill, in that the aerobic mode precedes the anaerobic mode. Although both modes are important, anaerobic decomposition exerts the greater and longer lasting influence in terms of associated fill characteristics.

2.4.1.9.1 Aerobic Decomposition. The greater part of decomposition that occurs directly after the wastes are buried is aerobic. It continues to be aerobic until all of the oxygen (O2) in the interstitial air has been removed. The duration of the aerobic phase is quite brief and depends upon the degree of compaction of the wastes, as well

as the moisture content since the moisture displaces air from the interstices. Microbes active during this phase include obligate as well as some facultative aerobes.

Because the ultimate end products of biological aerobic decomposition are “ash”, CO_2, and H_2O, adverse environmental impact during the aerobic phase is minimal. Although intermediate breakdown products may be released, their amounts and contribution to pollution usually are small.

2.4.1.9.2 Anaerobic decomposition. Because the oxygen supply in a landfill soon is depleted, most of the biodegradable organic matter eventually is subjected to anaerobic breakdown. This anaerobic decomposition is biologically much the same as that in the anaerobic digestion of sewage sludge. Microbial organisms responsible for anaerobic decomposition include both facultative and obligate anaerobes.

Unfortunately, the breakdown products of anaerobic decomposition can exert a highly unfavorable impact on the environment unless they are carefully managed. The products can be classified into two main groups: volatile organic acids and gases. Most of the acids are malodorous and of the short-chain fatty-acid type. In addition to chemical reactions with other components, the acids serve as substrates for methane-producing microbes.

The two principal gases formed are methane (CH_4) and CO_2. Gases in trace amounts are hydrogen sulphide (H_2S), hydrogen (H_2), and nitrogen (N_2) (UNEP, 2001).

2.4.2 Methane Production on Landfill Areas

The generation of both municipal and industrial solid wastes has increased in parallel to rapid industrialization. Effective management of these wastes has become a major social and environmental concern. One of the important waste management strategies is co-disposal, which is a technique for the controlled disposal of industrial

wastes together with municipal solid wastes. The result of the commingling of wastes is a decrease in the cost of waste disposal (Erses & Onay, 2002).

Treatment and disposal of municipal, industrial and other solid waste produces significant amounts of methane (CH_4). In addition to CH_4, solid waste disposal sites (SWDS) also produce biogenic carbon dioxide (CO_2) and non-methane volatile organic compounds (NMVOCs) as well as smaller amounts of nitrous oxide (N_2O), nitrogen oxides (NOx) and carbon monoxide (CO) (Intergovernmental Panel on Climate Change [IPCC], 2006).

Landfills pass through four typical phases. The initial oxic phase is characterized by aerobic degradation. The oxygen within the landfill is soon depleted and an acid fermentation takes place, during which volatile fatty acids (VFAs) and alcohols are produced. The third, methanogenic, phase is characterized by methane production, and is the longest phase in a microbiologically active landfill. When the substrates from which methane is produced are depleted, oxygen may enter the landfill, and the final oxic degradation phase is established (Jonsson, Ejlertsson & Svensson, 2003).

The processes that produce gases in landfills are those associated with the microbiological decomposition of organic matter in the landfill. Farquhar (1989) has divided those processes into four phases: (1) aerobic; (2) anaerobic, non-methanogenic; (3) anaerobic, methanogenic, unsteady; and (4) anaerobic, methanogenic, steady. A short description of each phase as applied to a single mass of MSW after placement at time zero is presented in the following paragraphs (Cooper, Reinhart, Rash, Seligman & Keely, 1992).

In the aerobic phase, the landfill void spaces are filled initially with air (roughly 20% oxygen and 80% nitrogen). The oxygen present promotes aerobic bacterial decomposition, and inhibits anaerobe activity. As the oxygen is used up, CO_2 is produced at approximately equivalent rates so there is no net gas generation. However, the gas composition is changing (O_2 is being replaced with CO_2).

In Phase II, once the O_2 concentration is low enough, facultative and anaerobic processes begins. Initially, hydrolysis (an extra cellular, enzymatic process) occurs to reduce particulate organic matter to soluble components. This process requires significant moisture content, as well as physical contact between microorganisms and the waste. The waste gets broken down with various enzymes as follows:

Cellulose --- (cellulase) ---> glucose
Protein --- (protease) ---> amino acids
Starch --- (amylase) ---> glucose
Fats --- (lipase) ---> fatty acids

During this hydrolysis stage there is no gas production. However, as soon as the sugars and organic acids are formed, they are used by the microbes through a variety of metabolic pathways to produce simpler organic acids, water, carbon dioxide, ammonia, and even hydrogen (H_2). During this acid fermentation stage, CO_2 production occurs very rapidly. According to Farquhar (1989), different investigators have reported gas compositions as high as 50-70% CO_2 after 11 to 23 days, or even 90% CO_2 after 40 days. Methane (CH_4) production begins in the third phase; CO_2 rates decline and H_2 production ceases.

The duration of Phase III has been reported as being from 180 to 500 days, but as Farquhar (1989) points out, those studies were at less than optimal conditions and so the duration of phase III could be much shorter.

During Phase IV, the steady methane generation phase, gas of constant composition is produced at a steady rate. The composition has been reported as 50 percent CH_4 to 66 percent CH_4 with the balance being primarily CO_2. For illustrative purposes, stoichiometric equations for the above processes (using glucose as the "waste") can be written as follows:

I. Aerobic decomposition of glucose (no net gas produced):

$$C_6 H_{12} O_6 + 6O_2 \text{ ------> } 6CO_2 + 6H_2O$$

II a. Hydrolysis: No gas production

II b. Anaerobic acid fermentation of glucose (CO_2 and H_2 gas produced):

$$C_6 H_{12} O_6 \xrightarrow[H_2O]{\text{----------}} CH_3 COOH + C_2 H_5 COOH + CO_2 + H_2 \text{ and}$$

$$C_6 H_{12} O_6 \xrightarrow[H_2O]{\text{----------}} C_3 H_7 COOH + 2CO_2 + 2H_2$$

III & IV. Methane fermentation of glucose (CO_2 and CH_4 produced)

$$C_6 H_{12} O_6 \xrightarrow[H_2O]{\text{----------}} 3CO_2 + 3CH_4$$

The overall reaction for solid waste of arbitrary composition is as follows,

$$\mathbf{C_vH_wO_xN_yS_z} + [v - (w/4) - (x/2) + (3y/4) + (z/2)]\mathbf{H_2O} \text{ -----> } [(v/2)+(w/8)-(x/4)-(3y/8)-(z/4)]\mathbf{CH_4} + [(v/2)-(w/8)+(x/4)+(3y/8)+(z/4)]\mathbf{CO_2} + y\mathbf{NH_3} + z\mathbf{H_2S}$$

The ability of microorganisms to oxidize methane has been known since 1906, when Sohngen first isolated an organism capable of growing on methane as a carbon source. Methane generated by methanogenic bacteria within sanitary landfills has been well documented and has been implicated in several fires, explosions, and deaths in recent years (Mancinelli, Shulls & Mckay, 1981).

Methanogens play an important role in the degradation of organics, but this group is generally sensitive to heavy metals. In fact, only Methanobacterium bryantii BKYH, a copper resistant methanogen has been reported. According to Jarrell and Saulnier, zinc and copper have a strong inhibitory effect on methanogenesis (Methanobacterium thermoautotrophicum Marburg, Methanobacterium formicicum, Methanospirillum humgatei JFl and Methanosarcina barkeri MS) at l-10 $mg.1^{-1}$. Although a large amount of waste containing heavy metals is dumped in landfill sites, methanogenesis in the sites increases continually up to approximately the 7th

year from the start of dumping and reduces gradually there after (Mori, Hatsu, Kimura & Takamizawa, 2000).

Heavy metals affect the growth, morphology and metabolism of microorganisms of soils through functional disturbance, protein denaturation, or the destruction of the integrity of the cell membrane (Mohanty, Bharati, Deepa, Rao & Adhya, 2000).

Investigations on the biosorption mechanism of heavy metals show that the metal ions are deposited by adsorption to the functional groups present on the cell wall. Dead as well as living cells are used in the removal of metal ions (Nourbakhsh, Kiliçarslan, Ilhan & Ozdağ, 2002).

The toxicity of a heavy metal to anaerobic bacteria depends upon a number of factors, including chemical form, bioavailability, and the presence of bacterial species that are resistant to or can detoxify the metal (Kuo & Genthner, 1996).

The sources of heavy metal contamination include: vehicle emissions, mining, smelting, metal plating/finishing operations, automobile battery production, disposal of industrial waste, fertilizers, pesticides and fly ash from incineration/combustion processes (Majid & Argue, 2001).

The major sources of heavy metals in landfills are the co-disposed industrial wastes, incinerator ashes, mine wastes and household hazardous substances such as batteries, paints, dyes, inks, etc (Erses & Onay, 2002).

The toxic battery components of major concern are cadmium, lead, and mercury. Batteries have been the largest source of cadmium and mercury in MSW (US EPA, 1998).

The most common heavy metals in landfills are iron, cadmium, copper, zinc and nickel. The solubility of metals in leachate depends on the pH, the redox potential, and the solubility of the deposited metal species, concentration of complexing agents

(NH_3/NH_4^+, humic acids) and ion strength. Metal solubility in the leachate increase as pH decreases. Under methanogenic conditions, soluble metals precipitate as insoluble sulfides, carbonates, hydroxides and possibly phosphates in landfills. However, in the presence of sulfides, most of the heavy metals except chromium form extremely insoluble sulfide salt (Erses & Onay, 2002).

The acidogens responsible for acidogenesis are generally considered to be less sensitive to environmental conditions, e.g. toxicant concentrations, as compared to methanogens. However, Hickey et al. (1989) have speculated that some trophic group(s) or organisms within the anaerobic consortia of digesters might be more severely inhibited by a pulse addition of heavy metals than the methanogenic populations (Lin & Chen, 1999).

Effect of metal toxicity depends on pH. Since most methanogenic bacteria function in a pH range between 6.7 and 7.4 (Bitton, 1994), pH did not adversely the biogranules' activity.

Inhibition of anaerobic digestion of high organic wastes, for example, livestock and dewatered sewage sludge, is often caused by a high ammonia concentration. A high NH_4 concentration is toxic for anaerobes. McCarty reported that NH_4-N concentrations in excess of 3000 mg/ l were expected to be toxic at any pH value (Tada & others, 2005).

2.4.2.1 Effects and characteristics of heavy metals

2.4.2.1.1Lead. Lead in the environment is mainly particulate bound with relatively low mobility and bioavailability. Lead does, in general, not bioaccumulate and there is no increase in concentration of the metal in food chains. Lead is not essential for plant or animal life.

In general, inorganic lead compounds are of lower toxicity to microorganisms than are trialkyl- and tetraalkyllead compounds. There is evidence that tolerant

strains exist and that tolerance may develop in others. Lead compounds are in general not very toxic to microorganisms and lead compounds have contrary to mercury and chromium compounds not been used as biocides.

2.4.2.1.2 Mercury. Mercury is a peculiar metal. Most conspicuous is its fluidity at room temperature, but more important for the possible exposure of man and the environment to mercury are two other properties.

Under reducing conditions in the environment, ionic mercury changes to the uncharged elemental mercury which is volatile and may be transported over long distances by air.

Mercury may be chemically or biologically transformed to methylmercury and dimethylmercury, of which the former is bioaccumulative and the latter is also volatile and may be transported over long distances. Mercury is not essential for plant or animal life. Mercury and its compounds are toxic to humans. The toxicity varies among the different types of mercury. Generally, organic forms are much more toxic than the inorganic forms.

Mercury is toxic to microorganisms. Inorganic mercury has been reported to have effects at concentrations of the metal in the culture medium of 5 µg/liter, and organomercury compounds at concentrations at least 10 times lower than this /WHO 1991/. Organomercury compounds have been used as fungicides. These effects are often irreversible, and mercury at low concentrations represents a major hazard to microorganisms.

2.4.2.1.3 Cadmium. Cadmium and cadmium compounds are, compared to other heavy metals, relatively water soluble. They are therefore also more mobile in e.g. soil, generally more bioavailable and tend to bioaccumulate. Cadmium is not essential for plant or animal life.

Cadmium is readily accumulated by many organisms, particularly by microorganisms and molluscs where the bioconcentration factors are in the order of thousands.

Cadmium is toxic to a wide range of microorganisms as demonstrated by laboratory experiments. The main effect is on growth and replication.

4.2.2.1.4 Chromium. Chromium occurs in a number of oxidation states, but Cr (III) (trivalent chromium) and Cr (VI) (hexavalent chromium) are of main biological relevance. There is a great difference between Cr (III) and Cr (VI) with respect to toxicological and environmental properties, and they must always be considered separately. Chromium is similar to lead typically found bound to particles. Chromium is in general not bioaccumulated and there is no increase in concentration of the metal in food chains. Contrary to the three other mentioned heavy metals, Cr (III) is an essential nutrient for man in amounts of 50 - 200 μg/day. Chromium is necessary for the metabolism of insulin. It is also essential for animals, whereas it is not known whether it is an essential nutrient for plants, but all plants contain the element.

Hexavalent chromium is in general more toxic to organisms in the environment that the trivalent chromium. Almost all the hexavalent chromium in the environment is a result of human activities. Hexavalent chromium is toxic to microorganisms; a property utilized in chromium-based biocides. In general, toxicity for most microorganisms occurs in the range of 0.05 - 5 mg chromium/kg of medium. Trivalent chromium is less toxic than hexavalent. The main features are inhibition of growth and inhibition of various metabolic processes such as photosynthesis or protein synthesis (European Commission, 2002).

4.2.2.2 Inhibition / Toxic Concentration Levels. Due to the in which heavy metals take part in complex-type reactions with ammonia, carbonates and sulfides, it has been difficult to define a particular total heavy metal concentration which is

inhibitory or toxic . Table summarizes some information found in the literature (European Commission, 2002).

Table 2.6 Soluble heavy metal concentrations inhibitory to the anaerobic digestion process

Heavy Metal	Soluble Concentration, mg/L
As	0.5- 1.0
Cd	0.01-0.02
Cr	1.0-1.5
Cu	0.5-1.0
Ni	1.0-2.0
Zn	0.5-1.0

CHAPTER THREE
MATERIALS AND METHODS

3.1 Experimental Setup Used For the Study

In the experimental part of the study, glass jars of 1L capacity are used simulating the municipal solid waste landfills. The caps of the jars were holed and gas exit hoses are fixed. The surrounding of the each cap is closed with silicone to prevent gas leak. Plastic sponges are placed into the bottom of the jars to collect and separate the leachate produced from the solid part. The schematic configuration of these reactors is shown in Figure 3.1.

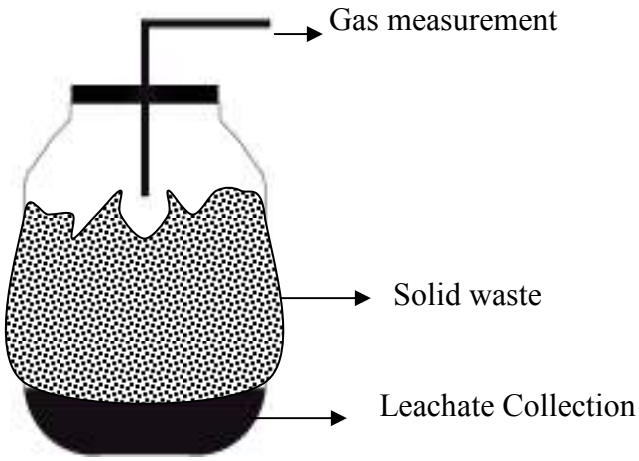


Figure 3.1 Reactor configuration.

Total gas production from the system is measured by liquid displacement method and the methane content of the gas composition is measured by using Drager Pac EX2. The reactors are placed into the incubator and operated under 35º during the study. The systems have been operated for 15 weeks and the analysis in leachate is completed after the waste is removed from the reactors.

Solid waste is obtained from Uzundere Composting Plant of Izmir Municipality which is operated by IZKA Ltd. Company. As soon as the solid waste transferred to the laboratory, it is screened under the 1.5 cm sieve and homogenized. Water content, organic matter content, TOC_d, TN_d, and total heavy metal content of the

waste is determined immediately. In addition, to determine the solubility of waste heavy metals; EPA 1310 Extraction Procedure is applied to the waste samples. Also, Tessier Sequential Extraction is followed to introduce the distribution of heavy metals among the bounding fractions. During the initial analysis the waste is stored in the fridge at 4ºC.

Three different initial heavy metal concentration of waste is used for the experimental study. One of these is the original heavy metal concentrations of the solid waste obtained from composting plant. Dissolvable heavy metal concentrations of wastes are used as the concentration data, since Turkish Hazardous Waste Control Regulation classifies the waste according to these values as it is explained in Appendix 11A.

To reach the lower heavy metal concentrations, the waste obtained from composting plant is diluted by addition of clean bread, potato and zucchini pieces. The material used for dilution is grounded and sieved under 1.5 cm previously. The properties of dilution waste are also determined.

To obtain higher concentrations in waste mix, heavy metal salts are dissolved in the distilled water and allowed to be absorbed by dry bread chunks. After these preparations, solid waste from composting plant is mixed with heavy metal containing bread, and normal zucchini and potato waste to obtain desired higher heavy metal concentration.

The heavy metal salts used in the reactor studies are as follows: $Pb(NO_3)_2$, $NiSO_4.7H_2O$, $CuSO_4.5\ H_2O$, and $ZnCl_2$.

Three reactors are operated for each of the three initial heavy metal concentrations. The averages of the data obtained from each reactor are given in results section.

3.2 Methods

The analysis applied in the study are water content (WC), organic matter content (OM), pH, TOC_d, TN_d, total heavy metal (Ni, Cu, Pb, Zn) analysis and Tessier Sequential Extraction procedure for determining the form distribution of heavy metals.

The methods and the analytical procedures used are summarized in Table 3.1. The dissolvable organic carbon and dissolvable nitrogen analysis are done in the elutriates obtained according to the procedure described in Turkish Hazardous Waste Control Regulation- Appendix 11A, which is adopted from EPA Method 1310 Extracting Procedure.

Table 3.1 Analytical methods used

Parameters	Method	Procedure
Water Content (WC)*	Standard Methods, AWWA 1981	The sample dried at 105°C overnight and differences between the initial and final weights are used to determine the water content. MEMMERT Loading Model 100-800 drying oven is used for the experiments.
Organic Matter Content (OM)*	Standard Methods, AWWA 1981	The dried sample combusted at 550°C for 2 hours and differences between the initial and final weights are used to determine the organic matter content of dry portion. MEMMERT LM 100-800 furnace is used for the experiments.
pH*	EPA Method 9045C	20 grams of sample is mixed with 20 ml of distilled water for 5 minutes and centrifuged at 4000 rpm for 10 minutes. The pH value of the supernatant is measured. NUVE NF 815 centrifuge and HANNAH HI 8314 pH meter is used for the experiments.
Total Gas	Liquid Displacement Method	Distilled water containing 2% H_2SO_4 and 10% NaCl is used as liquid which is not allowing any gas to be trapped in.
Methane	Direct measurement	Methane was analyzed by Drager Pac EX2 methane gas analyzer.
Heavy Metals (Pb, Cu, Ni, Zn)	EPA Method 3050B	Dried samples are digested according to EPA3050B and the heavy metals are determined in the extracts by using ICP-OES.
TOC_d	EPA 1310	Dried samples are extracted according to the EPA 1310 and the results are determined in the supernatant by using DOHRMAN DC – 190 / 832 – 932 TOC Analyzer.
TN_d	EPA 1310	Dried samples are extracted according to the EPA 1310 and the results are determined in supernatant by using MERCK nitrogen kits and Nova 60 Photometer

* The analysis are duplicated

Tessier Sequential Extraction is an analytical method describing the bounding forms of the metals in a matrix. The forms are heavy metal and their features can be explained as follows:

- **Exchangeable form**: Metals extracted during this step are those which are weakly absorbed and retained on the soil surface by relatively weak electrostatic interaction and metals that can be released by ion-exchange processes.

- **Bound to carbonates:** These metals can be co-precipitated with the carbonates present in many soils. This fraction is easily effected by pH changes. The exchangeable and bound to carbonates fractions are loosely bound and labile materials and these are most available for plant uptake.

- **Bound to Fe - Mn Oxides**: These are the metals in reducible state that are bound to iron/manganese oxides and they are unstable under reducing conditions. Changes in redox potential induce the dissolution of these oxides and release absorbed trace metals.

- **Oxidizable.** These are the metals bound to organic matter. The degradation of organic matter under oxidizing conditions can lead to a release of soluble trace metals bound to this component.

- **Residual.** These are the metals bound within the crystal matrix and they are not expected to be released under normal conditions in nature.

To determine these five fractions mentioned above Tessier Sequential Extraction protocol is applied to the waste samples.

(i) ***Fraction 1, Exchangeable****;* 1 gram of dried and powdered solid waste sample was extracted at room temperature for 1 hour with 8 ml of magnesium chloride solution (1 M $MgCl_2.6H_2O$) with continuous agitation. (80 rpm, in shaking incubator). The samples were then centrifuged at 2500 rpm for 30 minutes; the supernatant was carefully removed to a test tube to analyze the exchangeable forms of metal concentrations. The residue was washed with 8 ml of pure water; the

sample was centrifuged as above, this second supernatant was carefully removed and discarded.

(ii) ***Fraction 2, Bound to Carbonates;*** The residual from ***(i)*** was extracted with 40 ml of 0.11 molar acetic acid in shaking incubator at 80 rpm for 16 hours. The samples were then centrifuged at 2500 rpm for 30 minutes; the supernatant was carefully removed to a test tube to analyze the *bound to carbonates* fraction of metal concentrations. 20 ml of pure water was used to wash the samples and centrifuged as above.

(iii) ***Bound to Iron-Manganese Oxides;*** A volume of 40 ml of 0.5 M hydroxylamine hydrochloride (acidified with 2 M HNO_3 to pH 2) was added to each tube and the process of shaking, centrifugation and washing was repeated. The supernatant analyses gave the reducible form of the metal concentrations.

(iv) ***Bound to Organic Matter;*** In this fourth step of the procedure, 10 ml of hydrogen peroxide (%30 H_2O_2) was added to each sample and the samples were left to stand at room temperature for 1 hour, and then placed into a water bath at 85^0C for a further hour. Then the peroxide was evaporated to reduce the volume to about 1 ml. A further 10 ml of hydrogen peroxide was added and left in water bath for another 1 hour and peroxide was evaporated again to near dryness. After cooling the samples, 50 ml of ammonium acetate (acidified to pH 2 with HNO_3) was added to each tube and the shaking, centrifugation and washing process described above was repeated.

(v) ***Residual.*** The difference between the total metal concentration and the sum of the four fractions mentioned above gave the metals found in residual fraction.

In addition to the fore mentioned analysis dried and granulated solid waste samples are extracted according to the EPA 1310 Extraction Procedure and total dissolvable heavy metal concentrations are determined.

Gas measurements are done two times a week during the week days and leachate sampling and analysis are done at the end of the study. The average of the data obtained from the three reactors used for each of the three different heavy metal concentration and the results are given in the following section.

CHAPTER FOUR
RESULTS AND DISCUSSION

4.1 Results

Determination of general properties of the waste used in the study is the preliminary analysis completed in the experimental part. After the placement of waste mixtures into the reactors total gas production and methane content of the total gas have been measured until the study is ended. The leachate produced during the experiments is measured volumetrically and its properties are determined at the end of the study. Below, general properties of the wastes, gas measurements, and leachate properties of the reactors are given under the related sub-titles.

4.1.1 General Properties of Solid Waste Samples

General properties of the waste used in the study are determined and the results are given in Table 4.1.

Table 4.1 General properties of waste samples

Waste Type	Water Content,%	Organic Matter Content, %	TOC_d, mg/L	TN_d, mg/L
Solid Waste from Compost Plant	60	37	119200	4900
Bread	26	70	242400	3100
Potato	81	16	38200	980
Zucchini	94	5	340	20

Heavy metals in the waste samples are also determined. Heavy metal content of clean bread, potato, and zucchini can not be determined since the concentrations are below the detection limits. In Table 4.2 heavy metal concentrations found in solid waste collected from composting plant is given. The dissolvable portion of the total heavy metals and the distribution of heavy metals according to the bounding fractions are also given in the same table.

4.1.2 Heavy Metal Concentrations and other Waste Properties in the Reactors

The "Dissolved Portion" column, which can be seen in Table 4.2, shows the water soluble heavy metals present in the solid waste according to the procedure given in Turkish Hazardous Waste Control Regulation Appendix 11A (THWCR-App.11A). In this appendix, the wastes are categorized according to their soluble contaminant contents.

Table 4.2 Total heavy metals, dissolved portions, and their distribution according to bounding fractions in composting plant solid waste

Heavy Metal	Total Heavy Metal*	Dissolved Portion **	Distribution According to the Bounding Fractions***				
	ppm dw	mg/L	Exchangeable, ppm dw	Bound to Carbonates, ppm dw	Bound to Fe-Mn Oxides, ppm dw	Oxidizable, ppm dw	Residual, ppm dw
Cu	143.1	0.523	3.77	3.20	16.53	68.81	50.82
Ni	3.7	0.015	0.04	0.23	0.29	1.35	1.80
Pb	92.3	0.08	0.32	1.14	5.51	43.73	41.63
Zn	289.0	4.53	2.12	89.11	46.72	43.35	108.38

*Total acid digestion, EPA Method 3050B, ** Extraction procedure, EPA Method 1310 and Turkish Hazardous Waste Control Regulation Appendix 11A, *** Tessier sequential extraction procedure

The categories and the related soluble heavy metal concentrations in Regulation are given in Table 4.3 to compare the values which are obtained by using composting plant solid waste.

Table 4.3 The limit values for dissolvable waste contaminants in THWCR-App.11A

Heavy Metal	**Waste Disposal Categories**		
	Dispose as Inert Waste, mg/L	**Dispose as Non-Hazardous Waste, mg/L**	**Dispose as Hazardous Waste, mg/L**
Cu	≤0.2	0.2-5.0	5-10
Ni	≤0.04	0.04-1.0	1-4
Pb	≤0.05	0.05-1.0	1-5
Zn	≤0.4	0.4-5.0	5-20

As can be seen from the values in Tables 4.2 and 4.3 solid waste obtained from composting plant can be categorized as 'Non-Hazardous' due to the dissolved

portions of Cu, Pb, and Zn, and can be categorized as ‘Inert’ due to the dissolved portion of Ni.

By using the limit values given in Table 4.3; clean bread, potato, and zucchini are added to the solid waste to obtain lower dissolvable heavy metal concentrations, and for obtaining higher concentrations $Pb(NO_3)_2$, $NiSO_4.7H_2O$, $CuSO_4.5H_2O$, and $ZnCl_2$ is dissolved in distilled water and absorbed by dry bread and added to the solid waste.

‘Inert Waste’ composition is obtained by applying dilution to the solid waste. Dilution rate is decided to be 12 for obtaining the inert waste standard for Zn in the Regulation. One portion of solid waste is mixed with 11 portion clean vegetables that contain 45% bread, 27.5 % zucchini and 27.5 % potato. The clean vegetable mixture water content and organic matter content are equal to the water content and organic matter content of the solid waste which are 60% and 37%, respectively.

‘Hazardous Waste’ composition is also obtained by addition of vegetables and bread to the waste obtained from composting plant. To obtain the same organic matter content and water content in all of the reactors one portion of solid waste and eleven portion of clean waste mixture is also used for this reactor. In that case, first bread is dried overnight at 75ºC in the oven. Then 366.0 mg $CuSO_4.5H_2O$, 197.5 mg $NiSO_4.7H_2O$, 75.0 mg $Pb(NO_3)_2$, and 391.0 mg $ZnCl_2$ are dissolved in 100 ml distilled water. Each reactor used in the study contains 500 g of waste mixture. Since the water content of the final waste mixture will be 60%, the dry waste weight in one reactor will be 150 g. That means the reactor contains 62 g bread with a 26% water content -which is equal to the 16 ml-. 100 ml of prepared heavy metal solution is added to the 287.5 g of dried bread and 26% water content is obtained. Then 45% heavy metal containing bread, 27.5 % zucchini and 27.5 % potato are mixed and they are added to the solid waste. After the homogenization of the waste mix, the dissolvable heavy metal content of the waste will be the highest values given in THWCR-App.11A for hazardous waste category. In Table 4.4, initial total heavy

metal concentrations and dissolvable heavy metal concentrations in three different reactors and their waste properties can be seen.

Table 4.4 Initial dissolvable heavy metal concentrations and waste properties in the reactors.

Parameter		**Reactor 1 Inert Waste**	**Reactor 2 Non-Hazardous Waste**	**Reactor 3 Hazardous Waste**
Cu	**Dissolvable, mg/L**	0.043	10	0.523
	Total, ppm dw	11.92	112	143.1
Ni	**Dissolvable, mg/L**	0.0013	0.015	4
	Total, ppm dw	0.308	3.7	44.3
Pb	**Dissolvable, mg/L**	0.007	5	0.08
	Total, ppm dw	7.69	57.66	92.3
Zn	**Dissolvable, mg/L**	0.377	20	4.53
	Total, ppm dw	24.08	224	289
Water Content, %		60	60	60
Organic Matter Content,%		37	37	37
TOC_d, mg/L		119639	119200	119639
TN_d, mg/L		1939	4900	1939

4.1.3 Total Gas Production in the Reactors and its Methane Content

The total gas production rates in the reactors during operation time and methane contents of the gas are given in Table 4.5. Cumulative gas productions in the reactors are as follows; 189 L in Reactor I, 176 L in Reactor II, and 144 L in Reactor III. The

maximum methane content of the total gas is 52%, 47% and 1% for the reactors I, II, and III, respectively.

Table 4.5 Gas production rates and methane contents of the gas generated from the reactors

Days	Reactors					
	RI Inert Waste		RII Non-Hazardous Waste		RIII Hazardous Waste	
	Total Gas, mL/h	Methane Content, % v	Total Gas, mL/h	Methane Content, % v	Total Gas, mL/h	Methane Content, % v
1	36	12	24	12	18	0,0
4	56	16	42	20	37	0,0
8	74	21	66	24	56	0,0
11	96	21	86	21	54	0,5
15	102	25	86	27	51	0,5
18	108	36	80	32	48	0,5
22	104	36	78	30	55	1,0
25	106	39	78	35	56	0,5
29	104	35	86	33	61	1,0
32	102	34	94	25	69	1,0
36	102	30	92	30	68	1,0
39	102	32	110	29	75	1,0
44	104	38	108	38	77	0,5
46	102	36	110	25	80	1,0
50	94	31	106	28	67	1,0
53	96	34	114	36	77	1,1
57	88	36	102	37	72	1,0
60	78	34	106	28	65	1,0
64	76	41	88	39	69	1,0
67	78	40	82	39	71	1,0
71	78	41	78	42	72	1,0
74	72	50	72	43	64	1,0
78	66	52	68	43	58	0,5
81	60	50	52	41	60	1,0
85	54	51	34	44	54	1,0
88	44	51	24	47	49	1,0
92	32	48	24	30	41	1,0
95	26	33	20	24	35	1,0
99	24	29	20	22	37	0,5
103	28	27	20	22	36	0,5
105	28	24	20	13	39	1,0

4.1.4 Properties of Leachate Generated from the Systems

At the end of the 15 weeks of operation time the reactors are brought to the room temperature (21ºC) and the waste contents are emptied. The leachate at the bottom of the each reactor is measured volumetrically and its properties are analyzed. The results of the tests are given in Table 4.6.

Table 4.6 Leachate properties of the reactors

Parameters	Reactors		
	RI Inert Waste	**RII Non-Hazardous Waste**	**RIII Hazardous Waste**
Leachate Volume, mL	40	48	45
pH	7.86	7.44	3.81
TOC, mg/L	2922	1292	400
Cu, mg/L	0.2	0.8	44
Ni, mg/L	0	0.3	12
Pb, mg/L	0.1	0.4	14
Zn, mg/L	3	4.8	37

4.1.5 Final Properties of the Waste in the Reactors

After the operational period the waste in the reactors are emptied and final properties are determined. The results are given in Table 4.7.

Table 4.7 Final properties of the waste in the reactors

Parameter	Reactor 1 Inert Waste	Reactor 2 Non-Hazardous Waste	Reactor 3 Hazardous Waste
Cu, mg/L**	0.037	0.497	6.78
Ni, mg/L**	*	*	2.12
Pb, mg/L**	*	0.01	242
Zn, mg/L**	0.2	3.8	11.6
Water Content, %	53	53	58
Organic Matter Content,%	24	26	35
TOC_d, mg/L	85332	88440	104004
TN_d, mg/L	1300	2860	1886

* Under detection limits and will be accepted as zero. ** Dissolvable portion

Total heavy metals in the reactors are also analyzed and their bounding fractions are determined according to the Tessier Sequential Extraction procedure. The findings are given in Table 4.8.

Table 4.8 Heavy metals in the waste and their bounding fractions after the experimental study completed

Reactor	Heavy Metal	Total Heavy Metal	Distribution According to the Bounding Fractions**				
		ppm dw	Exchangable, ppm dw	Bound to Carbonates, ppm dw	Bound to Fe-Mn Oxides, ppm dw	Oxidizable, ppm dw	Residual, ppm dw
RI Inert	Cu	10.6	0.16	1.02	3.31	3.71	2.4
	Ni	0.2	*	0.03	0.02	0.02	0.13
	Pb	7.4	0.20	1.0	0.86	3.7	1.64
	Zn	18.4	0.04	3.7	3.4	4.84	6.42
RII Non-Hazardous	Cu	81.8	*	0.02	6.36	34.52	40.92
	Ni	2.4	0.01	*	0.27	1.19	0.93
	Pb	41.8	0.12	3.92	14.66	13.64	9.46
	Zn	141	0.12	21.36	27.82	38.76	52.94
RIII Hazardous	Cu	119.4	1.05	2.0	11.62	47.6	57.13
	Ni	27.5	*	*	4.06	7.06	16.38
	Pb	77.4	0.32	0.98	4.78	37.6	33.72
	Zn	166	0.04	71.04	36.56	44.76	13.6

*Under detection limits and will be accepted as zero, ** Tessier sequential extraction procedure

4.2 Discussion

In this part, the finding of the study will be discussed under the subtitles of gas production, leachate generation and properties, general properties of the waste, and heavy metal content of the waste in the reactors.

4.2.1 Gas Production in the Reactors

The total gas production and its methane content for the reactors RI, RII, and RIII are presented in Figures 4.1, 4.2, and 4.3, respectively.

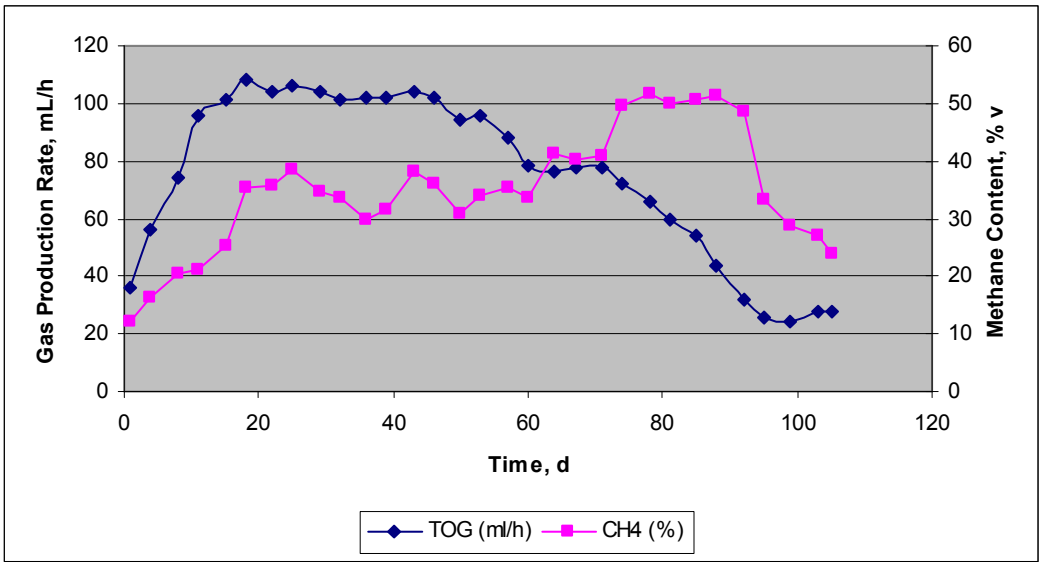


Figure 4.1 Total gas production and its methane content for RI (Inert Waste).

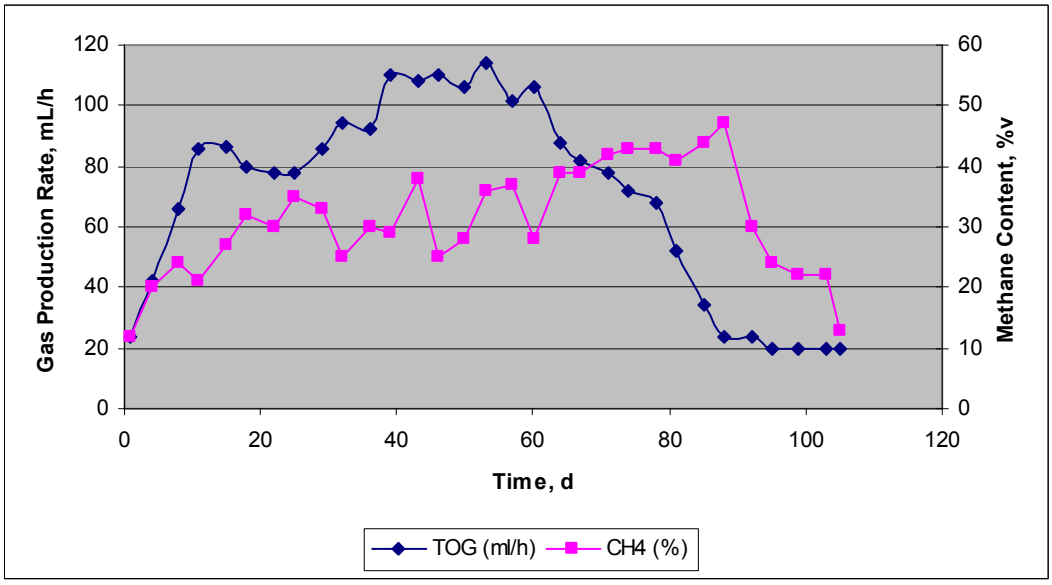


Figure 4.2 Total gas production and its methane content for RII (Non- Hazardous Waste).

As can be seen from the figures, the gas production rate (GPR) over 100 mL/h is achieved in RI at the 15th day of the experiments while it is seen in RII at the 39th day. The maximum gas production rate has seen in RII as 114 mL/h, and the reactor could stay in this mode for 21 days and the decline in GPR has started to be seen. But RI's maximum GPR is lower than RII as 108 mL/h which could stay in this mode for

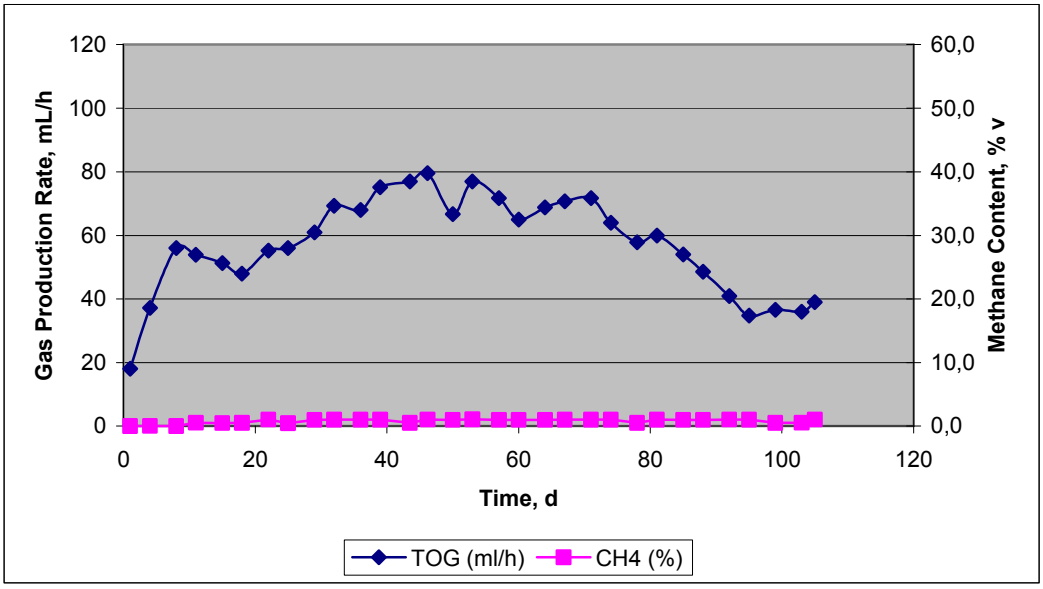


Figure 4.3 Total gas production and its methane content for RIII (Hazardous Waste).

30 days. As a result of this the total gas productions in RI and RII are 189 L and 176 L, respectively. Even if the RIII produced 144 L of gas the methane content of the gas produced is the major observation of this study. In RI, average of 52% of the total gas is CH_4, where it is 47% in RII and only 1% in RIII. The cumulative methane productions from the reactors are determined as 66 L for RI, 56 L for RII, and only 1.2 L for RIII. That means the gas produced in RIII is mainly carbon dioxide.

4.2.2 Leachate Properties of the Reactors

The leachate generations in the reactors are close to each other. The most important data related with the leachate properties is pH, which is highly acidic in RIII (Hazardous Waste). As a result of acidic conditions in this reactor the heavy metal concentrations in leachate are much higher than the reactors RI and RII. This acidic condition can be the reason of the low methane content of the gas produced in RIII. There is a slight difference in pH values of leachates from RI (7.86) and RII (7.44). But it can be said that pH effects the degradation of carbonaceous organic materials negatively and lower TOC values are detected in RII and RIII.

4.2.3 Changes in General Waste Properties after the Experiment

It is seen that the water content of RIII decreased only 3% during the experiment. That is much lower than the water lost in RI and RII which are equal to 12% and this is an indication of an absence in effective biological anaerobic decomposition.

When the initial and final organic matter contents, TOC_d and TN_d values are compared, it is recognized that reductions in these parameters are poor in RIII. Except TN_d, reductions in RI are higher than RII and RIII. The initial TN_d of RII is much higher, so the final concentration of that parameter is still high.

According to the data, the changes in soluble heavy metal levels are depending on the type of the metal. The bounding forms of the metals, which are the subject of the next subtitle, may help to explain such behavior.

4.2.4 Changes in Total Concentrations and Bounding Forms of Heavy Metals in Waste

Since initial and final forms of heavy metals in waste might be an important factor of inhibition in the reactors this property is discussed here. Figure 4.4 presents the initial heavy metal distribution in the reactors RI, RII, and RIII.

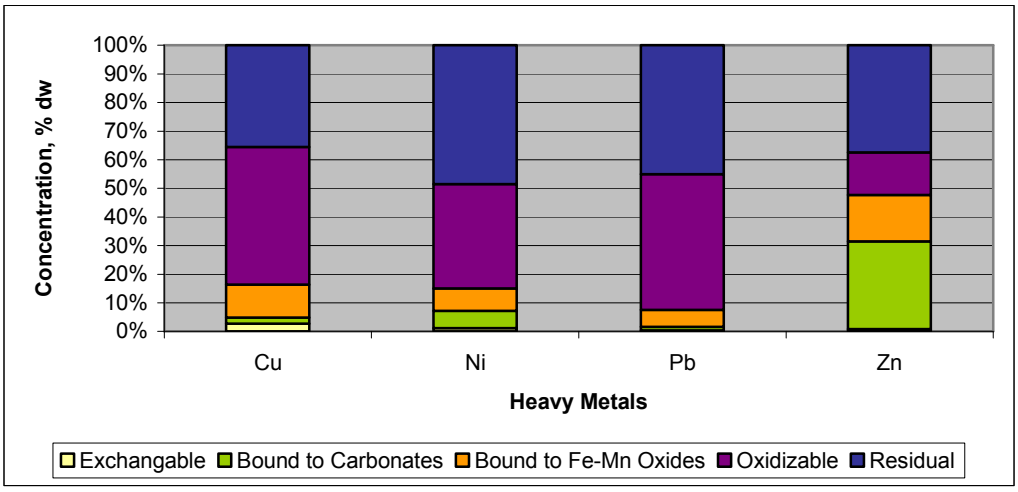
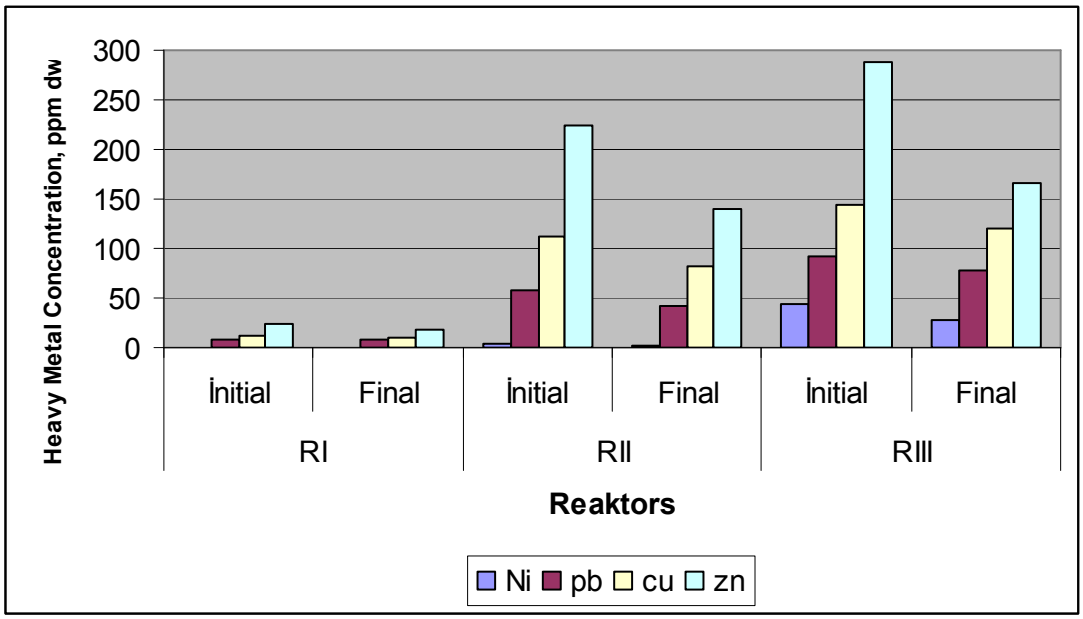


Figure 4.4 Bounding forms of initial heavy metal concentrations in waste.

As can be seen from the figure Cu, Ni, and Pb concentrations are mostly distributed in oxidizable and residual forms where Zn is distributed in all forms except exchangeable form. According to this distribution Zn is expected to be dissolved in higher levels than the other heavy metals under changing pH conditions and possible oxidizing-reduction reactions occur during biodegradation.

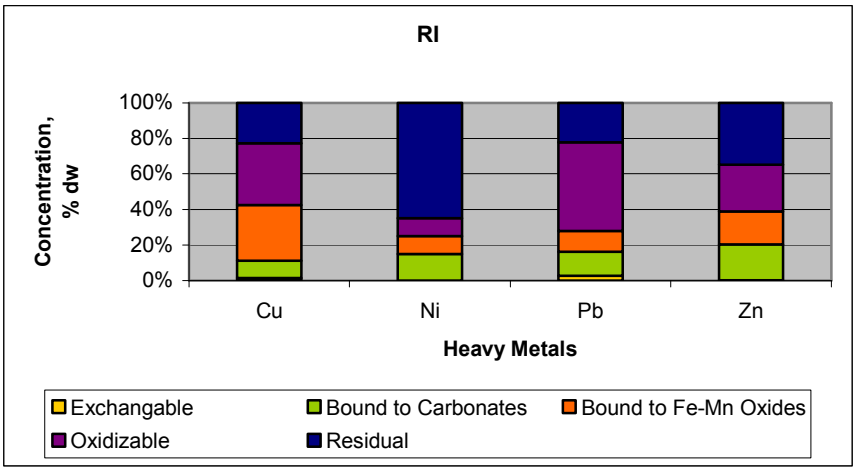
The anaerobic biodegradation occurred in the rectors changed the total heavy metal concentration in waste content of the reactors. In Figure 4.5 the concentration changes in heavy metal content of the wastes in the reactors can be seen.

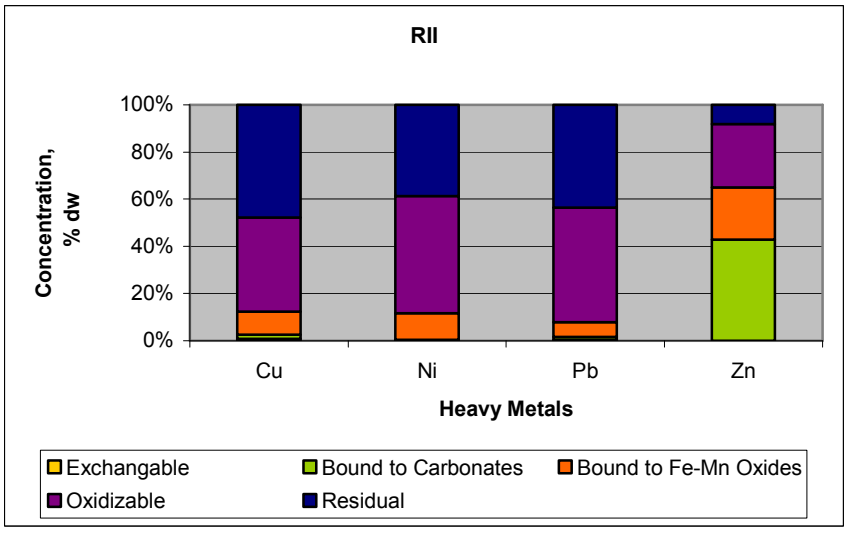
Figure 4.5 Changes in heavy metal concentrations in the reactors.



As it is explained in materials and methods section, the heavy metal concentration in RIII is increased by addition of metal salts and the total “dissolvable” heavy metal content of this reactor is higher than RII, not the total heavy metal concentration. As it is seen in Figure 4.5 biodegradation and the acidic conditions reduced the total heavy metal concentration in reactors. As it is expected because of lower pH values in RIII leaching of many of the heavy metals has occurred in this reactor and the total heavy metal concentration of the waste has decreased. Decreases in heavy metal concentrations of RI and RII are also significant but they are lower than the decrease in RIII.

When we look at the changes in forms of the metals in the reactors the results can be shown as in Figure 4.6.





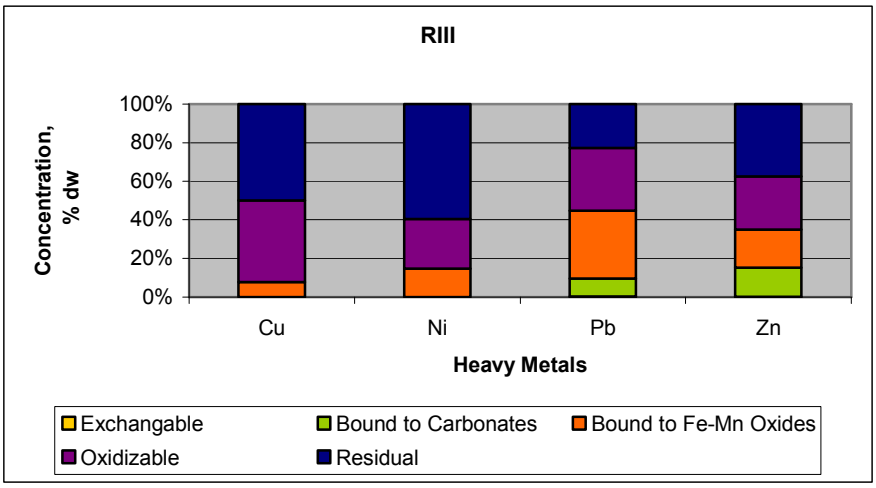


Figure 4.6 Form distributions of heavy metals in waste after the experimental study completed.

When Figures 4.5 and 4.6 evaluated together it is seen that total heavy metal reduction in Zn has occurred leaching of heavy metals from all of the bounding forms of this metal in all of the reactors. While residual fraction is increasing for Ni in RI, Cu and Pb has leached primarily from the more soluble forms; namely exchangeable and carbonates. In RII, it is seen that the residual and oxidizable forms have increased which means that the mobility of soluble forms has carried out during the decomposition in this reactor. RIII is the reactor with the highest heavy metal mobility for Cu, Ni, and Zn because of acidic conditions occurred in this reactor. Pb is not dissolved since its only soluble salt is $Pb(NO_3)_2$ which is probably turned out to be another form during the experiment and stayed immobile.

Another observation of the study is; the addition of soluble heavy metal salts into the waste body can be immobilized by the waste material and can be bounded. But it should be considered that the waste body should not be reached to the acidic conditions since leachate may have high concentrations of heavy metals.

CHAPTER FIVE
CONCLUSION

The effect of heavy metal concentration in solid waste on methane generation in landfill areas is studied in the content of the thesis. Three different solid waste mixes are prepared with different initial heavy metal concentrations. Gas production and methane content of the gas, leachate properties, and form distributions of heavy metals are determined either by direct measurement or by using analytical methods. The conclusions of the study according to the findings can be summarized as follows;

- Heavy metal concentration in solid waste effects the gas production rate and methane content of the total gas produced. Higher concentrations of heavy metals cause lower gas production and lower methane content of the total gas.
- Dissolvable portion of heavy metals are much effective on gas production and methane content of the gas.
- Presence of high dissolvable heavy metal concentrations cause acidic conditions in waste body and only carbon dioxide is produced under anaerobic conditions since methanogenic bacteria needs alkali conditions to develop.
- If the initial heavy metal concentration is low or in acceptable levels metals are partially immobilized by the waste, since both alkali and methanogenic conditions can develop.
- If methane yield is considered in a landfill area it should not be allowed to be disposed of dissolvable heavy metals containing wastes in that area.
- Dissolvable heavy metals may leach and causes the trouble of advanced treatment of leachate.

REFERENCES

Cooper, C. D., Reinhart, D. R., Rash, F., Seligman, D., & Keely, D., (1992). Landfill Gas Emission, Civil and Environmental Engineering Department University of Central Florida, July 31, 1992.

EPA, (1998). *An Analysis of composting as an environmental remediation technology*, (n.d.). Retrieved July 11, 2007, from http://www.epa.gov/epaoswer/non-hw/compost/analpt1.pdf

EPA, (1998). *An Analysis of composting as an environmental remediation technology*, (n.d.). Retrieved July 11, 2007, from http://www.epa.gov/epaoswer/non-hw/composting/basic.htm,

EPA, (2003). *Guidelines for the Sitting, Design and Management of Solid Waste Disposal Sites in the Northern Territory*, (n.d.). Retrieved July 11, from www.epa.gov

Erses, A. S., Fazal, M. A., Onay T. T., & Craig W. H., (2005). Determination of solid waste sorption capacity for selected heavy metals in landfills. *Journal of Hazardous Materials*, B121, 223–232.

Erses, A. S., & Onay T. T., (2003). In situ heavy metal attenuation in landfills under methanogenic conditions, *Journal of Hazardous Materials,* B99, 159–175.

European Commission, (2002). *Heavy metals in waste.* Retrieved September 15, 2007, from http://ec.europa.eu/environment/waste/studies/pdf/heavy_metalsreport.pdf

Intergovernmental Panel on Climate Change [IPCC], (2006). Guidelines for National Greenhouse Gas Inventories

http://www.ipcc-nggip.iges.or.jp/public/2006gl/pdf/5_Volume5/V5_3_Ch3_SWDS.pdf

Jonsson, S., Ejlertsson, J., & Svensson, B. H., (2003). Behavior of mono- and diesters of o-phthalic acid in leachates released during digestion of municipal solid waste under landfill conditions, *Advances in Environmental Research,* 7, 429–440.

Kınay, H. E., (2003). Development of cost effective and environmentally sound solid waste management systems, M.Sc. thesis, Department of Environmental Engineering, Dokuz Eylül University, (in Turkey)

Kuo, C. W., & Genthner, S. B. R., (1996). Effect of Added Heavy Metal Ions on Biotransformation and Biodegradation of 2-Chlorophenol and 3-Chlorobenzoate in Anaerobic Bacterial Consortia, *Applied and Environmental Microbiology*, p. 2317–2323.

Lin, C. Y., & Chen, C. C., (1999). Effect of Heavy Metals on the Methanogenic UASB Granule, *Wat. Res*. Vol. 33, No. 2, pp. 409±416.

Majid, A., & Argue, S., (2001). Remediation of heavy metal contaminated solid wastes using agglomeration techniques. *Minerals Engineering*, Vol. 14, No. I 1, pp 1513-1525.

Malkow, T., (2004). Novel and innovative pyrolysis and gasification technologies for energy efficient and environmentally sound MSW disposal. *Waste Management*, 24, 53–79.

Mancinelli, L. R., Shulls, A. W., & Mckay, C. P., (1981). Methanol-Oxidizing Bacteria Used as an Index of Soil Methane Content, *Applied and environmental microbiology*, Vol. 42, No.1, p 70-73.

Mohanty, R. S., Bharati, K., Deepa, N., Rao, R. V., & Adhya, K. T., (2000). Influence of Heavy Metals on Methane Oxidation in Tropical Rice Soils. *Ecotoxicology and Environmental Safety*, 47, 277±284.

Mori, K., Hatsu, M., Kimura, R., & Takamizawa, T., (2000). Effect of Heavy Metals on the Growth of a Methanogen in Pure Culture and Co culture with a Sulfate-Reducing Bacterium, *Journal of Bioscience and Bioengineering*, Vol. 90, No. 3, 260-265.

Mukherjee, B.A., Zevenhoven, R., Brodersen, J., Hylander, D.L., & Bhattacharya, P., (2004). Mercury in waste in the European Union: Sources, disposal methods and risks. *Resources, Conservation and Recycling,* 42, 155–182.

Municipal solid waste incineration the decision makers guide, (n.d.). Retrieved September 15, from, http://www.google.com.tr.

Nourbakhsh, M. N., Kiliçarslan, S., Ilhan, S., & Ozdağ, H., (2002). Biosorption of Cr6+, Pb2+ and Cu2+ ions in industrial waste water on Bacillus sp. *Chemical Engineering Journal, 85*, 351–355.

Resource Conservation and Recovery Act [RCRA], (2001). *RCRA Solid waste programs*, (n.d.). Retrieved September 15, 2007, from www.epa.gov/epaoswer/hotline/training/swprg.pdf

Solid waste disposal. (n.d.). Retrieved July 11, 2007, from http://encarta.msn.com/encyclopedia_761569634/Solid_Waste_Disposal.html

Tada, C., Yang, Y., Hanaoka, T., Sonoda, A., Ooi, K., & Sawayama, S., (2005). Effect of natural zeolite on methane production for anaerobic digestion of ammonium rich organic sludge. *Bioresource Technology,* 96, 459–464.

Tunç, E., (2005). The Recovery and Recycling Applications for Municipal Solid Wastes Generated in Izmir Metropolitan Area, M.Sc. thesis, Department of Environmental Engineering, Dokuz Eylül University, (in Turkey).

UNEP, (2001). Solid waste management. Retrieved July 11, 2007, from www.unep.or.jp/Ietc/Publications/spc/Solid_Waste_Management/Vol_I/14-Chapter8

UNEP, (2001). Solid waste management. Retrieved July 11, 2007, from http://www.unep.or.jpietcPublicationsspcSolid_Waste_ManagementVol_I20_21-Part3_Section-Chapter14-rev.pdf

Urban Development Sector Unit East Asia and Pacific Region, 1999. What a Waste: Solid Waste Management in Asia May 1999. *Conservation and Recycling.*