Nuray CEBECİ

M.S. Thesis In Environmental Engineering

July - 2011

REMOVAL OF THE HEAVY METALS IN THE MEDICAL WASTE INCINERATION ASH USING STABILIZATION MATERIALS

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APPROVAL PAGE

I certify that this thesis satisfies all the requirements as a thesis for the degree of Master of Science.

Ass. Prof. Dr. Sami GÖREN
Head of Department

This is to certify that I have read this thesis and that in my opinion it is fully adequate, in scope and quality, as a thesis for the degree of Master of Science.

Prof. Dr. Mehmet BORAT
Supervisor

Examining Committee Members

Prof. Dr. Mehmet BORAT

Ass. Prof. Dr. Sami GÖREN

Ass. Prof. Dr. Mustafa PETEK

Ass. Prof. Dr. Ferhat KARACA

Ass. Prof. Dr. Ali Ekrem MÜFTÜOĞLU

It is approved that this thesis has been written in compliance with the formatting rules laid down by the Graduate Institute of Sciences and Engineering.

Nurullah ARSLAN
Director

July 2011

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Supervisor: Prof. Dr. Mehmet BORAT

Co-Supervisor: Ass. Prof. Dr. Sami GÖREN

ABSTRACT

Inaccurate management and disposal of medical wastes from health organizations threaten the environment and human health. In this study, medical waste incineration ashes (bottom ashes) transferred to ISTAÇ Medical Waste Incineration Plant at Kemerburgaz under the roof of Istanbul Metropolitan Municipality is used. In this study, the amount of metals that medical waste incineration ashes contain as pollutants are determined and activities are carried out to eliminate the heavy metals determined using the adsorption technique. Bentonite and klinoptilolite is used in the study as adsorbent. Separate trials are carried out for both adsorbent. Ashes were mixed with adsorbent material and small columns are created. This adsorbent-ash is tested in different amounts and accordingly the mixture providing optimum elimination was sought. Leachate is obtained by supplying pure water to columns. Each mixture used during trials are used for the second time and adsorption performance of adsorbents were monitored.

In general, the bottom ash contains metal at a higher level than the level specified in literatures in terms of CO metal and contains low level of metal in terms of As, Cd, Cr and Pb and contains same level in terms of Cu and Ni.

Keywords: Heavy metals, bentonite, zeolite, leachate, adsorption, medical waste incineration ash

TIBBİ ATIK YAKMA KÜLÜNDEKİ AĞIR METALLERİN STABİLİZASYON MALZEMELERİNİ KULLANARAK GİDERİMİNİ SAĞLAMA

Nuray CEBECİ

Yüksek Lisans Tezi – Çevre Mühendisliği
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Tez Danışmanı: Prof. Dr. Mehmet BORAT

ÖZ

Sağlık kuruluşlarından kaynaklanan tıbbi atıkların hatalı yönetim ve bertarafları çevreyi ve insan sağlığını tehdit etmektedir. Bu çalışmada, İstanbul Büyükşehir Belediyesi’ne bağlı Kemerburgaz’daki İSTAÇ Tıbbi Atık Yakma Tesisi’nden gelen tıbbi atık yakma külleri (taban külleri) kullanılmıştır. Çalışmada tıbbi atık yakma küllerinin kirletici olarak içerdiği metallerin miktarları belirlenmiş ve tespit edilen ağır metallerin adsorpsiyon tekniği ile giderimi sağlanmaya çalışılmıştır. Çalışmada adsorbant olarak Bentonit ve Klinoptilolit kullanılmıştır. Her iki adsorbant için ayrı deneyler yapılmıştır. Küller adsorbant malzemesi ile karıştırılarak küçük kolonlar oluşturulmuştur. Bu adsorbant-kül karışımları değişik oranlarda denenmiş, böylece optimum giderimi sağlayan karışımı bulmak amaçlanmıştır. Kolonlara saf su verilerek sızıntısuyu elde edilmiştir. Deney esnasında kullanılan her bir karışım 2. Defa kullanılarak adsorbantların adsorpsiyon performansı takip edilmiştir.

Genellikle taban külü içinde sadece Co metali bakımından literatürden daha yüksek mertebede metal içerirken Cu ve Ni bakımından eşdeğerde ve As, Cd, Cr ve Pb bakımından çok düşük oranda metal içermektedir.

Anahtar Kelimeler: Ağır metaller, bentonit, zeolit, sızıntı suyu, adsorpsiyon, tıbbi atık yakma külü

DEDICATION

Finally, I wish to dedicate this thesis to my husband, Serkan CEBECİ and my parents Elif - Halil KIRKAÇ. Thanks for the support, understanding, encouragement and love that they have given to me throughout my life.

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SYMBOL/ABBREVIATION	
BOİ	Biological Oxygen Need
EPA	Environmental Protection Agency
HMW	Healthcare Medical Waste
ICP	Inductively Coupled Plasma
ISTAC	Istanbul Metropolitan Municipality Enterprises for waste management
kcal	Kilo Calorie
kj	Kilo Joule
KOİ	Chemical Oxygen Need
kPa	Kilo Pascal
LNG	Liquid Natural Gas
mg	Milligram
MHz	Mega Hertz
mmSS	Millimeter Water Column
MW	Mega Watt
Nm^3	Normal Cubic Meter
ppb	Parts Per Billion
ppm	Parts Per Million
PVC	Poly Vinyl Chloride
S/S	Stabilization / Solidification
TAEK	Turkish Atomic Energy Authority
TAKİ	Medical Waste Control Regulation
VOC	Volatile Organic Compound
WHO	World Health Organization

CHAPTER 1

INTRODUCTION

1. INTRODUCTION

Medical wastes include both wastes of domestic quality and also wastes of hazardous quality. Medical waste in particular has increased greatly since hospitals use relatively more disposable items, such as syringes, cutlery, food trays, bed pans, etc. (Morrison, 1992). It can consist of infectious, radioactive, and toxic substances from hospitals, laboratories, and clinics. These include sharps (syringes and needles), blood products, human tissues, body parts, pharmaceuticals, cytotoxins, and heavy metals, in addition to the items of general use such as paper, food, plastics etc. According to WHO (World Health Organization), the waste produced by hospitals carries a higher potential for infection and injury than any other kind of waste (A.V.D. Bos, 2002). These wastes are disposed of by using some methods such as landfilling, incineration, sterilization, etc. If these wastes are disposed of by incinerating, it is complied with the principles signified in the hazardous wastes control regulation (Medical Waste Control Regulation, O.G. Date 22.07.2005). If these wastes are sanitary landfilled, they are disposed of as signified in the medical waste control regulation. In the disposal of the wastes, the inevitable occurring of the leachate is important in terms of environment and human health. The leachate, which filters through solid wastes, occurs by exposing several events like chemical, biological and physical and it is collected from outside with the leachate collecting systems (ISTAC Co.Ltd Web Site). The leachate includes numerous elements and compounds arising from content of the solid wastes (ISTAC Co.Ltd Web Site). It also includes micro contaminants except organic and inorganic ions and metals (Armağan, 10-12 Oct 2001). The result of the leachate's discharging is that surface water and partly underground water can be polluted (Armağan, 10-12 Oct 2001). Pollution parameters differ according to the content of solid waste causing the formation of leachate. The metal concentration of leachate, which is formed by the wastes whose content of heavy metal is high, will accordingly high, as well. Poisonous metals (Pb, Cd, Co, etc.) that can cause the danger of toxic metal pollution in the environment reach the constitution via sources from which living beings utilize such as nutrients, water and air. (Henden, 19 Dec 2008). The pollution of these sources means that concentrations of these elements are over the acceptable limit values (Henden, 19 Dec 2008). The massive volume of the medical waste in many countries of the world is mostly reduced through incineration that leads to the generation of ash as a new type of waste (Javied. Sabiha, 2008). The combustion process destroys pathogens and reduces the waste volume by 95% and weight by 75% (Enger, 2004). The incineration of hospital wastes not only releases toxic gases (CO, CO_2, NO_2, SO_2 etc.) into the atmosphere but also leaves solid material as residue which makes bottom and fly ashes increase the level of heavy metals, inorganic salts and organic compounds in the environment (R.Ibanez, 2000). Some methods are used for the refinement of dangerous wastes which include heavy metals. Stabilization and solidification (S/S) is a refinement alternative that is carried out for different types of industrial wastes before storing. It is appropriate especially for dangerous wastes which include heavy metals (Malviya, 2006).

1.1. THE SUBJECT AND OBJECTIVE OF THE STUDY

In disposal of medical wastes, despite the storage method is used because it is more economical, because of the land can be used to flush and storage areas are thought to be limited the amount of waste must be diminished to the lowest levels. However, because of the high cost of medical waste recycling, non-possibility of recovery of all waste and lack of cleanliness and purity on materials recovered, combustibility at a rate of 99.02%, non-combustibility at a rate of only 0.97%, heating value of 3400 -9300 kcal / kg and hygiene reasons, incineration process -a multi-functional intermediate removal method- is preferred. Because in incineration, the infected materials decay at high temperatures, volume reduction takes place above a rate of 90%, the amount of waste sent to landfill area reduces, less pre-treatment process required with respect to other removal methods and a significant decrease provided at on-site incineration. (Li, 1993)

1.2. PURPOSE AND SCOPE OF STUDY

Bottom ash is an un-avoidable by-product of incineration which is concentrated of heavy metals that can be used for the land filling and block making. Metals are not destroyed during incineration and are often released into the environment, along with ash, in more concentrated and dangerous way (Javied. Sabiha, 2008). High temperature combustion evaporates some toxic metals from waste products consisting of batteries, paints and certain plastics. The tiny metal particles suspended in air increase the risk of inhalation related diseases (Greenpeace, 2005). The most important industrial activities, which are effective in the diffusion of heavy metals to the environment, are production of cement, iron and steel industry, thermal plants, production of glass and facilities of garbage and waste mud’s incineration (G.Pacyna, 2007). In this study, concentration levels of heavy metals (Hg, Cd, Tl, Sb, As, Pb, Cr, Co, Cu, Mn, Ni) in the leachate, which can occur by using incineration ash of medical waste coming from the institution of waste incineration that is operated by ISTAC Co. Ltd., an establishment of Istanbul Metropolitan Municipality, are determined; the removal of heavy metals in different pHs is shown by trying zeolite and bentonite from natural absorbents and the most appropriate stabilization conditions, which provide removal, are determined.

1.3. MEDICAL WASTES

Health-care waste consists primarily of pathological, infectious, chemical, pharmaceutical, and domestic wastes as well as sharps that have been contaminated with blood, infectious agents, tissues, organs, etc. (Alagöz, 2008). World Health Organization defines the medical wastes as both all wastes that are generated by health-care organizations, laboratories and research organizations and all kinds of wastes that emerge from small and scattered sources such as medical care processes at home (Kabacıoğlu, 2006). HMW can include general refuse wastes, like paper, flowers, food, plastic cups, as well as laboratory and pharmaceutical chemicals (alcohols, disinfectants, etc.), and infectious wastes like contaminated sharps, human blood and blood products, tissues and body parts, cultures, etc. (Environmental Protection Agency (EPA), 1990). Medical wastes should be classified according to their source, typology and risk factors associated with their handling, storage and ultimate disposal (Alvim-Ferraz M.C.M., 2003). Environmental European Agency identifies ‘‘specific hospital waste’’ and ‘‘other hospital waste’’, and Portuguese Legislation settles the following four types:(i) Group I— wastes similar to municipal ones; (ii) Group II— nonhazardous medical wastes that do not require specific treatment and can be considered as similar to municipal wastes; (iii) Group III— medical wastes with biological risk that must be pre-treated before elimination as municipal wastes; (iv) Group IV—specific medical wastes with compulsory incineration (Alvim-Ferraz M.C.M., 2003). When about 75-90% of the wastes which occur in the health-care activities are compared to domestic wastes, they are not risky, in other words they are "general" medical wastes. They usually result from the administrative/managerial functions of medical organizations and include the wastes that occur during the maintenance of building and outbuilding of the medical establishments. The remaining 10–25% of the medical wastes are described as hazardous wastes and they bring about various risks for health (ISTAC Co. Ltd., 2007).

According to USA Environmental Protection Agency's definition of medical waste, it is a solid waste that consists of processes of humans' or animals' diagnosis, treatment and vaccination, medical researches and examination of biological materials (Environmental Protection Agency (EPA), 1998).

1.4. WASTES RESULTED FROM HEALTHCARE ORGANIZATIONS

Wastes which result from healthcare organizations are divided into 4:

1. Wastes of domestic quality:
   a) General wastes,
   b) Package wastes,
2. Hazardous wastes.
3. Radioactive wastes.
4. Medical wastes:
   a) Infectious wastes,
   b) Pathological wastes,
   c) Sharp wastes (Özerol, 2002)

Healthcare organizations produce a large amount of infectious wastes resulted from medical procedures such as blood-contaminated surgical garment, human tissues and syringes. As well as the final disposal of these wastes, used bedclothes and other materials from experimental animals constitute important problems. In addition, toxic chemicals, expired medications, laboratory chemicals used in the analysis and the batteries that require special treatment for final disposal can be among the problematic wastes (Saad, 2003).

From the total of wastes generated by health-care activities, almost 80% are general waste comparable to domestic waste. The remaining approximate 20% of wastes are considered as hazardous materials that may be infectious, toxic or radioactive. The wastes and by-products cover a diverse range of materials, as the following list illustrates (percentages are approximate values):

- Infectious wastes -- cultures and stocks of infectious agents, wastes from infected patients, wastes contaminated with blood and its derivatives, discarded diagnostic samples, infected animals from laboratories, and contaminated materials (swabs, bandages) and equipment (disposable medical devices etc.)
- Anatomic -- recognizable body parts and animal carcasses.

Infectious and anatomic wastes together represent the majority of the hazardous waste, up to 15% of the total waste from health-care activities.

- Sharps -- syringes, disposable scalpels and blades etc.

Sharps represent about 1% of the total waste from health-care activities.

- Chemicals -- for example solvents and disinfectants; and
- Pharmaceuticals -- expired, unused, and contaminated; whether the drugs themselves (sometimes toxic and powerful chemicals) or their metabolites, vaccines and sera.

Chemicals and pharmaceuticals amount to about 3% of waste from health-care activities.

- Genotoxic waste -- highly hazardous, mutagenic, teratogenic or carcinogenic, such as cytotoxic drugs used in cancer treatment and their metabolites; and
- Radioactive material, such as glassware contaminated with radioactive diagnostic material or radio therapeutic materials;
- Wastes with high heavy metal content, such as broken mercury thermometers.

Genotoxic waste, radioactive matter and heavy metal content represent about 1% of the total waste from health-care activities.

The major sources of health-care waste are hospitals and other health-care establishments, laboratories and research centers, mortuary and autopsy centers, animal research and testing laboratories, blood banks and collection services, and nursing homes for the elderly. High-income countries can generate up to 6 kg of hazardous waste per person per year. In most of the low-income countries, health-care waste is usually not separated as hazardous and non-hazardous waste. In these countries, the total health-care waste per person per year is anywhere from 0.5 to 3 kg (WHO, 2010).

1.4.1. Domestic Wastes

1.4.1.1. General Wastes

These are the wastes that come from the parts where there are healthy people, the sections where the persons who are not sick are examined, the first aid areas, the administrative units, the cleaning services, the kitchen, warehouse and workshops (Medical Waste Control Regulation, O.G. Date 22.07.2005).

1.4.1.2. Package Wastes

They include wastes of uncontaminated, reusable, recyclable and regainable plastic, metal, glass and paper-pasteboard packages, which result from the unites (Medical Waste Control Refulation, O.G. Date 22.07.2005).

1.4.2. Hazardous Wastes

Hazardous wastes are the wastes that can be domestic or industrial rooted and are in the legally hazardous category and are taken additional precautions of human health and environment protection for their being collected, transported and removed. In other words, hazardous wastes are the wastes that occur depending upon the technological development and that are the wastes of industrial quality which threaten the environment and human health (Muşdal, 2007).

Figure 1.1 Hazardous Wastes [Atkasan, 2011]

1.4.3. Medical Wastes

a) Pathological wastes,
b) Infectious wastes,
c) Sharp wastes (Özerol, 2002)

1.4.3.1. Pathological Wastes

These are the human tissues (parts of body, placenta, experimental animals, and fetuses) (Şalva, 2001). They are suspected in containing sufficient quantities or concentrations of pathogens (bacterium, virus, parasite or fungus). They can be the reasons of lots of diseases.

Figure 1.2 Pathological Wastes [Berkeley National Laboratuary, 2011]

Infected wastes contain following types of wastes:

a) Contagious samples or cultures occurring in laboratory researches;

b) Wastes of surgery or autopsy carried out on the patients who catch contagious disease (for example: cleaning clothes and supply or equipment contacting with blood or other liquids of body);

c) Wastes of patients in quarantine (for example: urine, feces, sweat and clothes, blood or other body liquids of injured persons who are operated or persons who have contagious disease and quite dirty clothes);

d) Wastes of contagiously diseased persons who are on dialysis machine (for example: dialysis equipments, tubes, filters and towels, shirts, aprons, gloves and laboratory clothes that are thrown after one time use);

e) Animals that catch contagious disease in laboratories;

f) All kinds of material or equipment contacting with humans or animals that catch contagious disease (WHO, 2010).

1.4.3.2. Infectious Wastes

These are the wastes that are suspected in having pathogen; that consist of laboratory cultures, quarantines; that napkins (cleaning cloth), supplies or equipments, blood and other body liquids contacting with the persons who have contagious disease (Şalva, 2001)

Figure 1.3 Infectious Wastes [CP Lab Safety, 2011}

1.4.3.3. Sharp Wastes

These are the wastes that can cause pricking, piercing, graze and injuries like syringe and other all needles of subcutaneous entry, needle of serum set, needles of surgical suture, needles of biopsy, intraket, broken glass, ampule, lamella, broken glass tube and petri dishes (Veeken, 2000). They include syringe needle, other sharps that contains needle, lancet, lamella, glass pastor pipette and other broken glass materials which can cause pricking, piercing and graze injuries (Tıbbi Atıkları Kontrolü Yönetmeliği, R.G. Tarihi 22.07.2005).

Figure 1.4 Sharp Wastes [Berkeley National Laboratuary, 2011]

1.4.4. Radioactive Wastes

They occur as a result of usages of all kinds of radioactive material in different areas. With the rays of emerging from research laboratories, hospitals and some industrial establishments, they are wastes which cause danger for the environment and human health. (Karadağ, 2002).

Figure 1.5 Radioactive Wastes [Media Freedom International, 2011]

Wastes can be divided into two sub-categories: the wastes that emerge from nuclear power plants and studies about nuclear weapons have high radioactivity and wastes that emerge from research centers and hospitals have low radioactivity (Kabacıoğlu, 2006).

These kinds of wastes have to be stored in safer annihilation facilities than waste storing facilities (Kabacıoğlu, 2006).

1.5. PRODUCTION AMOUNT OF MEDICAL WASTES

Amount of Medical Wastes depends on various factors like waste management method of organizations, organization types, specifications of hospitals, reusability rate of health materials used and daily patient amount. Production rate of wastes may change both from country to country and also from region to region in a specific country (WHO, 1999).

According to World Health Organization, medical wastes compose 15-20% of all hospital wastes. Any difference in these percentages is directly parallel to level of development of a country (WHO, 1999).

1.6. MEDICAL WASTE CHARACTERIZATION

The calorific value, density and humidity values related to type of hospital wastes is given by Table 1.1.

Table 1.1 Characterizations of the Heath-Care Wastes (EPA, 1990; Kocasoy 1995)

Waste Type	High Calorific Value (dry basic) (kJ/kg)	Bulk Density as Fired (kg/m^3)	Moisture Content (Weight %)	Heat Value as Fired (kJ/g)
Human Bodies	18600-27900	800-1200	70-90	1860-8370
Plastics	32500-46500	80-2300	0-1	32500-46500
Absorbent pads	18800-27900	80-1000	0-30	13000-27900
Alcohols, disinfectants	25500-32500	800-1000	0-0,2	25500-32500
Infected animals	20900-37100	500-1300	60-90	2090-14900
Glass	0	2800-3600	0	0
Bedding, excrete	18600-20900	320-730	Eki.50	9300-18800
Paper	18600-27900	80-1000	0-30	13000-27900
Plastics, PVC, injectors	25500-46500	80-2300	0-1	22300-46500
Sharps, needles	140	7200-8000	0-1	140
Body liquids, wastes	0-23200	990-1010	80-100	0-4640

1.6.1. Harms of Medical Wastes In Terms Of Health

The health impacts of direct and indirect exposure to health-care wastes include carcinogenic, mutagenic, and teratogenic effects, reproductive system damage, respiratory, central nervous system effects, and many others. The hazardous nature of health-care wastes can be due to the fact that it contains infectious agents, toxic or hazardous chemicals or pharmaceuticals or sharps, or it is radioactive, genotoxic, etc. (Appleton, 2000).

1.6.1.1. Group under Threat

All individuals exposed to hazardous wastes are potentially at risk, including those affected through the direct contact with wastes every day of their working lives such as physicians, nurses, health-care personnel, and those outside the sources who either handle such wastes, or are exposed to it as a consequence of the improper management practices including the persons transporting these wastes, workers and operators of waste treatment and disposal facilities like the scavengers (Appleton, 2000).

1.7. MEDICAL WASTE MANAGEMENT

The basic elements of programs for the health-care waste management are given in the Table 1.2 (Christen, 1996).

Table 1.2 Basic Elements for the Management of Medical Wastes (Christen, 1996)

Comprehensive System **(a)** Assignment of responsibilities for waste management **(b)** Allocation of sufficient resources **(c)** Waste minimization, including purchasing policies and stock management practices **(d)** Segregation of waste into sharps, non-sharps infectious waste **(e)** Implementation of safe handling, storage, transportation, treatment and disposal options
Awareness and Training **(a)** Awareness raising of all staff about risks related to sharps and other infectious wastes **(b)** Training of health- care personnel regarding segregation practices **(c)** Training of waste workers regarding safe handling, storage and operation and maintenance of treatment technologies **(d)** Display of written instructions for personnel
Selection of Options **(a)** Identification of available centralized waste management and disposal resources **(b)** Choice of sustainable management and disposal options, according to: **i.** Affordability **ii.** environment-friendliness **iii** Efficiency **iv.** Worker's safety **v.** Prevention of the reuse of disposable medical equipment (e.g. syringes) **vi.** Social acceptability

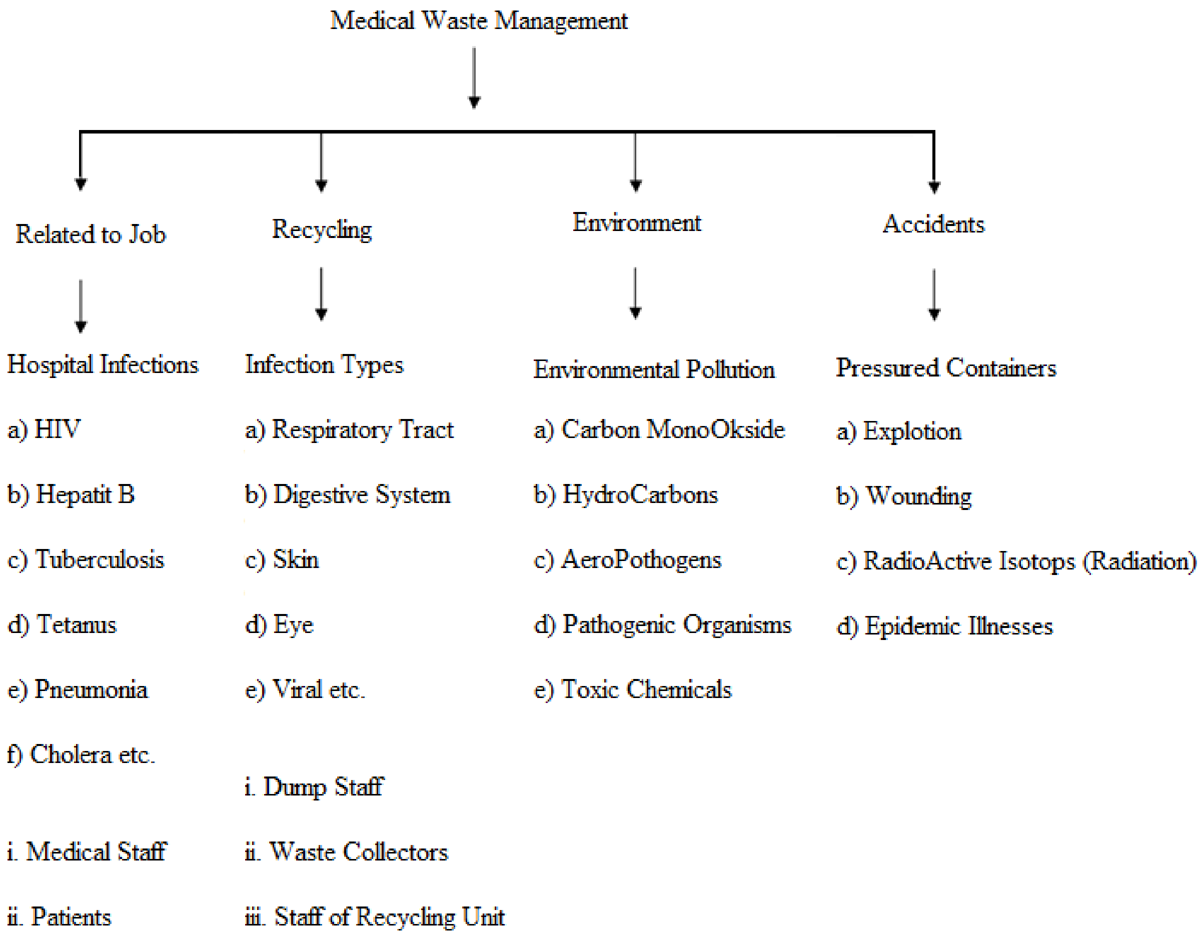

Figure 1.6 Possible Dangers Caused by Inappropriate Medical Waste Management (Patil and Shekdar, 2001)

1.7.1. Medical Waste Reduction

Waste minimization can be achieved through a variety of techniques, some as simple as product substitution, and some as complicated as a total process change requiring new training and equipment. The activities which are the heart of waste minimization are:

(a) Prevent waste generation,

(b) Reduce waste generation,

(c) Reuse wastes that has been generated, and

(d) Recycle wastes (Howarth, 2002)

1.7.1.1. Components of a Successful Waste Minimization Program

The efficient waste minimization programs can be accomplished by firstly identifying the important constituents of the minimization strategies. The key components of successful waste minimization programs are summarized in the following list:

a) Effective infection control procedures,
b) Pre-cycling of packaging,
c) Source separation and proper management of solid, medical and recyclable wastes,
d) Effective guidelines for clinical staff,
e) Effective "on-going" quality management, communication and training, and
f) Management commitment and leadership (Environmental Protection Agency (EPA), 1990)

1.7.2. Separate Collection of Medical Wastes

When collecting medical wastes red plastic bags with “ATTENTION! MEDICAL WASTE” expression and “International Biological Danger” emblem on both sides are used, which will be resistant against tearing, perforation, explosion and transportation and it will be produced from polyethylene raw material with original medium density and the base of the bag will be equipped with double seal and will have double thickness of 100 micron and minimum lift capacity of 10 kg (İbiş Mert, 2008).

Figure 1.7 International Medical Waste Bag and Medical Waste Emblem [Manufactures and Distributors of Plastic and Paper Goods, 2011]

The key to minimization and effective management of the health-care wastes is the identification of the wastes and segregation (separation) as it is mentioned above. The most appropriate way of identifying the categories of the health-care wastes is by sorting the wastes into color-coded plastic bags or containers. In addition to the color coding of the waste containers, the practices described in the following paragraphs are recommended. (Zeren, 2004)

Figure 1.8 Separation of wastes [Environmental Production Department, 2010]

1.7.3. On-Site Collection of Health-Care Wastes

Wastes should not be allowed to accumulate at the point of production. A routine program for their collection should be established as part of the health-care waste management plan. The ancillary workers in charge of waste collection should follow certain recommendations:

(a) Wastes should be collected daily (or as frequently as required) and transported to the designated temporary waste storage site.

(b) No bags should be removed unless they are labeled with their point of production (hospital and ward or department) and contents.

(c) The bags or containers should be replaced immediately with new ones of the same type (WHO, 1999)

Table 1.3 Indicators of Medical Waste (Çevre ve Orman Bakanlığı Sitesi, 2009)

Number of health facilities(1)	1.371
Number of health facilities collect their own medical waste	1.365
The amount of medical waste collected (tons/year)	57.078
The amount of medical waste per policlinic(2) (kg/person)	0,19
The amount of medical waste per inpatient(3) (kg/person)	5,42

(1) *Health facilities that produces large amount of wastes stated in TAKY Ek-1*

(2) *Policlinic is the patient applied for diagnosis and treatment*

(3) *Inpatients: Every patient that was prepared an “inpatient” plate*

1.7.4. Storage of Medical Wastes

Medical wastes in health organizations need to be stored until delivery to final disposal unit by authorities. Health institutions with a capacity of more than 20 beds must build their own temporary medical waste storage.

The properties of temporary storage facility shall be as follows:

(a) The temporary storage facility shall be constructed as an indoor area consisting of two sections. Medical waste shall be kept in the first section, while domestic quality waste shall be kept in the second section.

(b) The volume of temporary storage facility shall be large enough to hold at least two days’ collection of waste material.

(c) Floor and walls of the facility shall be sturdy and it shall be coated with a non-permeable material resistant to accumulation of microorganisms and dirt and also easy to clean and disinfect.

(d) The facility shall have a sufficient lighting system, a passive system of ventilation, and, in warmer areas, it shall be refrigerated.

(e) Doors of the facility shall either open outwards or they shall be sliding doors. Doors shall always be kept clean and painted. The door of the section that holds medical waste shall be painted in orange color and it shall bear on it, in a visible manner, the “International Biohazard Symbol” in black color and the expression “DİKKAT TIBBİ ATIK” (Attention Medical Waste)” also in black color.

(f) Doors of the facility when they are not being used, shall be kept always closed and locked; any person not authorized shall not be permitted to enter the facility. The facility and its doors shall be constructed so as to prevent entry of any animals.

(g) The interiors and doors of temporary storage facility shall be constructed with such dimensions as to permit the personnel in charge to work comfortably, and waste material to be unloaded, stored, and finally re-loaded, with ease.

(h) Temporary storage facility shall be constructed at such a location and in such a manner that the transport vehicles can easily access and dock.

(i) Temporary storage facility shall not be constructed near any places where there is intensive traffic of patients or humans in general, such as hospital gates or parking lots, or near places where food is stored, prepared, or sold.

(j) Cleaning and disinfecting of the storage section that holds medical waste shall be performed through use of dry methods. Once the waste in storage is removed, the section shall be cleaned, disinfected, and, where necessary, treated with insecticide. Any waste spilled due to tear or burst of a waste bag shall be collected using appropriate equipment, with any liquid waste thereof being concentrated by applying appropriate absorbent, and then placed again in red-colored plastic bags; finally the storage section, along with the equipment used thus, shall be promptly disinfected.

(k) In the section where domestic quality waste is held; there shall be a system of drainage with a grill connected to sanitation network, along with a water tap with (reasonably) high water pressure to facilitate cleaning of the section. Once the waste is removed; the section shall be cleaned, and, where necessary, it shall be disinfected and insecticide shall be applied.

(l) Cleaning equipment, protective apparel, waste bags, and containers shall be stored in places near the temporary storage facilities (Tıbbi Atıkları Kontrolü Yönetmeliği, R.G. Tarihi 22.07.2005)

Figure 1.9 Storage of Medical Wastes [Australian Nuclear Science & Technology Organisation, 2011]

1.7.5. Medical Waste Transportation

1.7.5.1. On-Site Transportation of the Health-Care Wastes

The health-care waste generator is responsible for the safe packaging and adequate labeling of wastes to be transported off-site and for authorization of its destination. Waste bags may be placed directly into the transportation vehicle, but it is safer to place them in further containers (e.g. cardboard boxes or wheeled, rigid, lidded plastic or galvanized bins). This has the advantage of reducing the handling of filled waste bags but results in higher disposal costs. These secondary containers should be placed close to the waste source (Nessa K., 2001)

Figure 1.10 The appropriate medical waste collecting vehicle [Government of the Common Wealth of Dominica, 2011]

1.7.5.2. Off-Site Transportation of the Health-Care Wastes

Before the transportation of wastes, dispatch documents should be completed, and all arrangements should be made between consignor, carrier, and consignee.

In Istanbul, Metropolitan municipalities, district municipalities or their assigns are collectively and successively responsible for the removal of medical wastes from interim stores or containers, transportation to disposal sites and disposal by incineration or final storage, as well as for training of the personal involved and documentation of these operations. Where necessary, the Ministry will provide cooperation in this respect to the municipalities. Medical waste materials shall be brought to final disposal sites in a safe manner without strewing around and straining of liquids and no transfer stations shall be used in transportation (Ministary Of Environment And Forestry of Turkey, 1993)

According to the Turkish Medical Waste Regulation, vehicles used for the transportation of medical waste materials:

- Should not contain compaction mechanisms,
- Should have totally enclosed loading tanks being of robust construction,
- Interior surfaces should be smooth and easily cleanable and not have sharp corners,

- Should bear the "International Clinical Waste" logo in front and in the rear,
- Exposed surfaces shall be painted orange (Figure 1.11),
- "Caution -Medical Waste" (Dikkat - Tıbbi Atıklar) shall be painted on the two sides in 20 cm tall lettering (Ministary Of Environment And Forestry of Turkey, 1993)

Figure 1.11 Off-Site Transportation of the Health-Care Wastes [ISTAC, 2011]

1.8. METHODS OF MEDICAL WASTE DISPOSAL

Medical wastes are disposed by incineration or regular storage process or they are turned into harmless forms by sterilization. Along with this, as the regulation on regular storage of wastes has entered into force when published on Official Gazette no. 27533 dated 26.03.2010, according to paragraph (c) of clause 2 of article 9 of the regulation, it is prohibited to accept in regular storage areas any medical wastes from medical and veterinary organizations which are defined as source of infection and which are not exposed to any process (Banar, 2011).

Due to the physical, chemical and biological features of wastes emerging from the medical facilities, the necessity of annihilation by separating them from other wastes occurs (Ege, 2009). There are many alternatives about wastes' being processed and disposed of. According to the risks and features of medical wastes, showing variety in terms of methods of process, price, usability and environmental effects brings out these alternatives (İbiş Mert, 2008).

- Incineration
- Chemical disinfection

- Thermal process
- Microwave sterilization
- Annihilation on land

1.8.1. Steam Sterilization (Autoclaving)

In this method, sterilization is provided with water steam at high pressure (Figure 1.12). Plastic bags of medical waste are put in cylindrical reactor. The process takes 30-90 minutes. 130-190^{o}C (minimum 121^{o}C) degrees and 100-500 kPa pressure are applied. After the process, the remaining waste is an inert matter and it is annihilated by being stored. The process is completely closed (Alpaslan, 2005; Albayrak, 21-22 May 2009; Bölükbaşı, 2006). Steam sterilization is a process making microorganisms inactive with humidity, heat and pressure (Küçükşahin, 2007). It is just the adaptation of standard process, which is used for the sterilization of reusable devices in the hospitals, for the annihilation of medical waste (Küçükşahin, 2007). In one bag, there may be quite different wastes and so it is difficult to adjust the sterilization conditions applied to each of them (İbiş Mert, 2008). Another disadvantage is that at the end of the process, wastes have a recognizable and disgusting appearance (Günaydın, 2001).

Figure 1.12 Autoclaving Plant [Symes, 11 March 2011]

1.8.1.1. Advantages and Disadvantages of Steam Sterilization

Below features and other similar features are the biggest advantageous of the system. (Türkmen, 2008).

- No chemicals are used.
- There is no incineration process.
- No harmful exhaust gas.
- No harmful waste leachate.
- No risk is present for the personnel working.
- It is automatic, has software controlled functionality and easy-to use style.
- High temperature for destroying bacteria.
- Volume reduction in the rate of approximately 1/8 after disintegration.
- Low operating costs compared to other systems.
- Number of workers required is low.
- No air-pollutant outputs.
- Practical to operate.
- All devices of the system can be tracked from a single center.

Advantages and disadvantages of the steam sterilization are presented in Table 1.4.

Table 1.4 Advantages and Disadvantages of Steam Sterilization (Alpaslan, 2005; Albayrak, 2009)

Advantage	Disadvantage
• more efficient and fast heat transfer • reduced volume by 70% • Appropriate for porous and penetrating wastes • No VOC • Not necessary extra drying process	• Not appropriate for chemical, pathological and radioactive wastes • No odor if there is no current of air

1.8.2. Incineration

Kiln Incineration is a dry oxidation process carried out at high temperatures and converts organic and other combustible wastes into inorganic and nonflammable materials. As a result, volume and weights of wastes will be reduced majorly. In general this process is used to process wastes that cannot be re-processed and turned into usable forms, wastes that can no longer be used or wastes that are not disposed to storage sites (Ege, 2009). Process flow is shown in Figure 1.13.

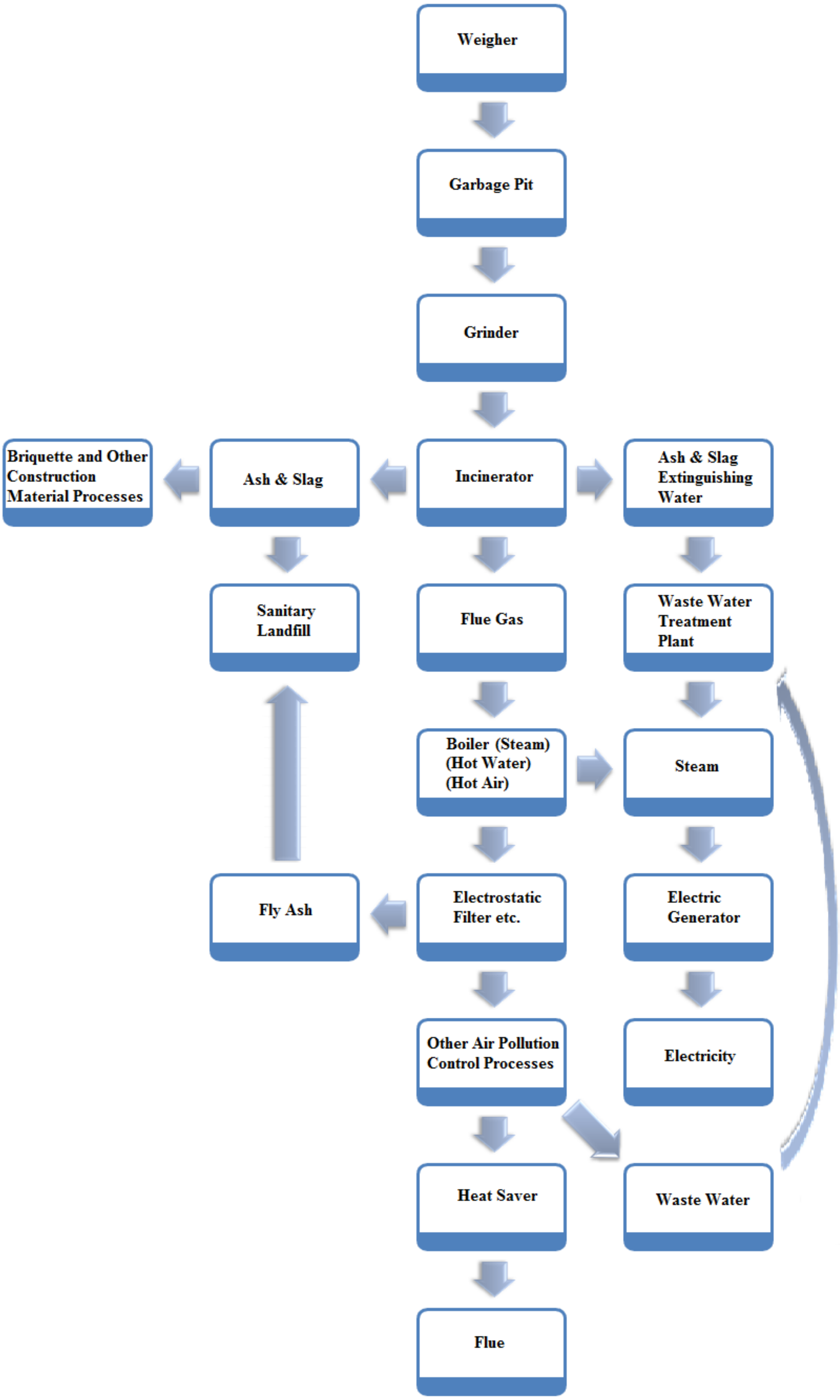

Figure 1.13 Incineration Plant Flow Chart (Borat, 2003)

Incineration equipment should be carefully chosen on the basis of the available resources and the local situation. Three basic kinds of incineration technology are of interest for treating health-care wastes:

(a) Rotary kilns operating at temperatures of 1200°C to 1600°C, capable of decomposition of genotoxic substances and heat-resistant chemicals,

(b) Double-chamber pyrolytic incinerators, which may be especially designed to burn infectious health-care wastes at temperatures of 800°C to 900°C,

(c) Single-chamber furnaces with static grate, burning temperature of 300°C to 400°C which should be used only if pyrolytic incinerators are not affordable, and

(d) Simple field incinerators with burning temperature of <300 °C (Diaz, 2002).

Figure 1.14 Rotary Kiln [Shangai Minggong Heavy Equipment, 2011]

In Turkey, incineration is the preferred method for the disposal of health-care wastes; however huge portion of the health-care wastes is disposed with domestic wastes. There are seven incineration facilities in Turkey, which are located in İstanbul, Ankara, Antalya, Sivas, Muğla and Kocaeli. In Istanbul, health-care wastes collected systematically by ISTAC from health establishments arc brought to the Storage Area in Kemerburgaz - Odayeri and discarded here by burning in the Health-Care Waste Incineration Plant, established in 1995, in high temperatures (Öztürk M. İ., 2002).

Hospital wastes cover various materials like paper and cartoon, plastic, liquid materials, anatomic parts, glass bottles, textile materials. There are three methods that can be used to dispose these materials by incineration:

- Pyrolysis,
- Starved air,
- Excess air (Brunner, 1988).

The most important condition required to carry out “pyrolysis” or “starved air” methods is the need for the waste to have organic character. Another condition is to be able to continue incineration without the need for extra fuel after target temperature is reached (autogenic incineration). If this condition cannot be met, there is no point in incineration practice below stoichiometric air volume and these are the weakest aspects of these two methods (Brunner, 1988).

Pyrolysis method is heating of organic materials in the absence of oxygen and disintegrating it to simple components. In a pyrloysis method that is applied accurately, the system does not release air at all or only releases the amount of oxygen required to supply the necessary temperature to carry out the process. With the impact of temperature, wastes to be disposed transform into solid wastes with flammable waste gas. The most important advantage of pyrolysis method is the need for low amount of oxygen. This allows reducing the size of the incinerator and also reduces fuel level necessary during operations. However it is very hard to meet the conditions required for this system. For example, it is very hard to prevent air from entering the incinerator without use of very expensive and complex methods (Brunner, 1988).

“Starved air” method is developed as an alternative to original pyrolysis method 60-90% of the amount of air calculated stoichiometrically is injected into the incineration room. Organic materials in the waste gas are incinerated by “excess air” method in the second incineration room. By supplying air to the first incineration in the amount lower than necessary, amount of particles carried in this room will be kept at low levels. This important feature of starved air method, the need for special emission control is eliminated. Another feature of this method is the ability to control the temperature of the incineration room (Brunner, 1988).

For disposing medical wastes by method of incineration, essentials stated under Regulation on Controlling Hazardous Wastes, articles related with incineration are followed.

1.8.2.1. Advantages and Disadvantages of Incineration

Table 1.5 Advantages and Disadvantages of Incineration (Esmen, 2008; Tutar, 2004)

Advantage	Disadvantage
• Variety of medical wastes • Pathologic wastes disappear in high heat • reduced volume by 75%	• Installation and operating is expensive because reaching high heat is expensive • Causes consist of carcinogenic gases like dioxin and furan • Causes air pollution when appropriate filtering system is not used

1.8.3. Chemical Disinfection

Despite that, solid and less hazardous medical wastes – microbiological cultures, sharps etc. – can be disinfected as chemically under the following limitations:

• Before the disinfection, breaking into pieces and/or grinding of the wastes is usually necessary. This process is almost the weakest ring of the chain since the disintegrators that are used often break down mechanically.

• It is necessary to have powerful disinfectants which have to be used by well-educated and sufficiently protected persons.

• Productive of disinfection is related to the managing conditions.

• Only the contacted surface of the whole solid waste is disinfected (Ege, 2009).

Chemical decontamination and disinfection is a technique, whose appropriate effect has been proved, for the treatment of certain medical wastes (Favero, 1991). For a beneficial chemical disinfection, infectious agents have to be in appropriate concentration with the disinfectant and appropriate period of time contact is needed (İbiş Mert, 2008). The wastes into which disinfectant can easily penetrate or the things, of which surfaces are dirty, are the wastes appropriate for the chemical treatment (İbiş Mert, 2008). Humidity and organic matters in the waste can reduce the effectiveness of some disinfectants (İbiş Mert, 2008). These units of practice are especially appropriate for the laboratory and small clinics (İbiş Mert, 2008).

1.8.3.1. Advantages and Disadvantages of Chemical Disinfection

Table 1.6 Advantages and Disadvantages of Chemical Disinfection (Alpaslan, 2005; Albayrak, 2009; Bölükbaşı, 2006)

Advantage	Disadvantage
• Can be used in disinfection of Infected body liquids, microbiological wastes, penetrating, reusable objects • Appropriate for small amounts • Reduced volume by 60-90%	• Both human and animal wastes and chemical wastes are not subject to chemical disinfection • Not appropriate for pathological wastes • Costs are variable. Chemical materials must be treated better to minimize the environmental effects which means additional cost

1.8.4. Microwave Sterilization

Microwave is the destruction of the microorganisms through the activity of waves with the frequency of 2 450 MHz and wavelength of 12.24. Wastes are disinfected with microwave heat at 94°C for a minimum exposure time of 25 minutes. Before the process, the wastes are shredded and granulated consequently to obtain the 80 per cent volume reduction. As the system is a totally closed system, it does not cause any emissions. Microwave technology has been approved and is commercially operable in Europe and the United States (WPA, 2001).

It is not appropriate for the wastes that include dry, quite wet and heavy metal (Günaydın, 2001).

Figure 1.15 Medical Waste Disinfection with Heat Conduction in Microwave Process [Obid, 2011]

1.8.4.1. Advantages and Disadvantages of Microwave Sterilization

Table 1.7 Advantages and Disadvantages of Microwave Sterilization (Alpaslan, 2005; Esmen, 2008; Tutar, 2004)

Advantages	Disadvantages
• Reduced volume by 80% • Wastes are drier than wastes resulted from autoclave sterilization	• Appropriate for wet wastes which contain certain proportion of water • Not available liquid blood and hazardous chemical materials • Before process the wastes must be put in special bags • First investment cost is higher than autoclave sterilization • Fragmentation of wastes in very small pieces cause fuzziness

1.8.5. Sanitary Landfill

Identifiable body tissue, cytotoxic wastes, pharmaceutical, laboratory or domestic chemicals, radioactive wastes, infectious wastes (only as exemption) are generally considered as not suitable for disposal at a landfill site. Soiled animal bedding, incontinence pads and other faeces/urine contaminated materials, health-care wastes which has been made safe by autoclaving in an autoclave, bulky, or large, items which are impractical to dispose of via incineration may be considered for landfilling with the prior approval of the local authority (Y., 2002).

Figure 1.16 Sanitary Landfill (Ekip Journal, 2011)

1.8.5.1. Advantages and Disadvantages of Sanitary Landfill

Advantages:

1- Where land is available, a sanitary landfill is usually the most economical method of solid waste disposal

2- The initial investment is low compared with other disposal methods

3- A sanitary landfill is a complete or final disposal method as compared to incineration and composting which require additional treatment or disposal operations for residue, quenching water, unusable materials, etc.

4- A sanitary landfill can be put into operation within a short period of time.

5- A sanitary landfill can receive all types of solid wastes, eliminating the necessity of separate collections.

6- A sanitary landfill is flexible, increased quantities of solid wastes can be disposed of with little additional personnel and equipment.

7- Sub marginal land may be reclaimed for use as parking lots, playgrounds, golf courses, airports, etc.

Disadvantages:

1- In highly populated areas, suitable land may not be available within economical hauling distance.

2- Proper sanitary landfill standards must be adhered to daily or the operation may result in an open dump.

3- Sanitary landfills located in residential areas can result in extreme public opposition.

4- A completed landfill will settle and require periodic maintenance.

5- Special design and construction must be utilized for buildings constructed on completed landfill because of the settlement factor.

Methane, an explosive gas, and the other gases produced from the decomposition of the wastes may become a hazard or nuisance problem and interfere with the use of the completed landfill (Gören, 2005).

1.8.6. Advantages and Disadvantages of Medical Waste Disposal Methods

Table 1.8 Advantages and Disadvantages of Medical Waste Disposal Methods (Visvanathan, 2006)

	Incineration	**Autoclave**	**Microwave**	**Chemical Disinfection**	**Plasma Pyrolysis**
Investment /Operating cost	High	Moderate	High	Low	High
Suitability Of the waste	Not for radioactive	All except Pathological	All except cytotoxic, radioactive	Liquid waste	All
Ease of Operation	No	Yes	Yes	Yes	No
Waste Volume reduction	Significant	Less	Significant	-	Significant
Odour Problems	Yes	Slight	Slight	Slight	-
Environmental friendly	No	Yes	Yes	No	Yes

1.9. PROCESSES CARRIED OUT AT ISTAC Co. Ltd. MEDICAL WASTE INCINERATION FACILITY AND TECHNOLOGY USED

In order to prevent air to enter, while supplying medical wastes to the kiln, supply tank is connected to a waste supply system that also serves as a disposal outlet.

Wastes are filled inside a rotating kiln by waste supply system. Sub-stochiometric ignition takes place inside the kiln. Ignition air at this part will be minimized and toxic gases are refined with minimum level of dust being produced (Öztürk H. İ., June 2009).

Inner surface of the rotating kiln is coated with refractory material and this kiln is equipped with a burner that keeps the energy level at minimum in order to allow continuous refining of toxic gases. Minimum retention time in the incinerator is 1 hour (Öztürk H. İ., June 2009).

In rotating kiln systems, less developed waste gas emission measures will be necessary compared to other system (Barton, 1991).

Inner part of rotating kilns is cylinder type kilns that are coated with refractory brick and that can rotate around its horizontal axis. The waste is directly transferred into the rotating kiln and excess method is used (Barton, 1991).

Rotating Kiln has a capacity of 1 ton/hour (for wastes with 3,500 kcal/kg calorific value). Calories of wastes that can be burned are min. 2,000 kcal/kg and max. 4,540 kcal/kg. Calorific density of the facility is 3,500,000 kcal/hour (4.07 MW). The rotating kiln has a volume of 27.5 m3 and length of 7.5 m and a diameter of 2.73 m. Rotating speed can be set and it is in the range of 0-12 cycle/hour (Öztürk H. İ., June 2009).

Grate following incineration process enables full burning. Exhaust gas produced inside the rotating kiln and on the grate following incineration passes from a narrow pipe and is transferred into the second incineration room. Turbulence inside the pipe enables gases to mix well and this is a pre-condition for complete incineration of gases. Second incineration room is equipped with a support burner in order to ensure that temperature is maintained at minimum. Retention period is minimum 1.5 seconds at 1200 °C in order to ensure that exhaust gases burn completely (Öztürk H. İ., June 2009).

In the facility of ISTAC The Istanbul Metropolitan Municipality Enterprises for waste management at Medical Waste Incineration Facility - Odayeri and Medical Waste

Landfill Site - Odayeri Köyü Kemerburgaz – ISTANBUL, medical waste incineration and electricity production is made (Öztürk H. İ., June 2009).

Figure 1.17 ISTAC Co. Ltd. Medical Waste Incineration Plant [ISTAC, 2011]

The facility has a capacity to burn 24 tons of medical wastes daily and works in 3 shifts and 24 hours a day with required technical team and equipment in order to carry out waste disposal works. All units can be controlled automatically by 2 operators with 2 terminal computers and 8 cameras and 6 monitors are used at various points (Öztürk H. İ., June 2009).

Wastes are burned between 1000 °C and 1200 °C inside a kiln with special refractory and wastes are decreased 95% by volume and 75% by mass as the result of incineration (Öztürk H. İ., June 2009).

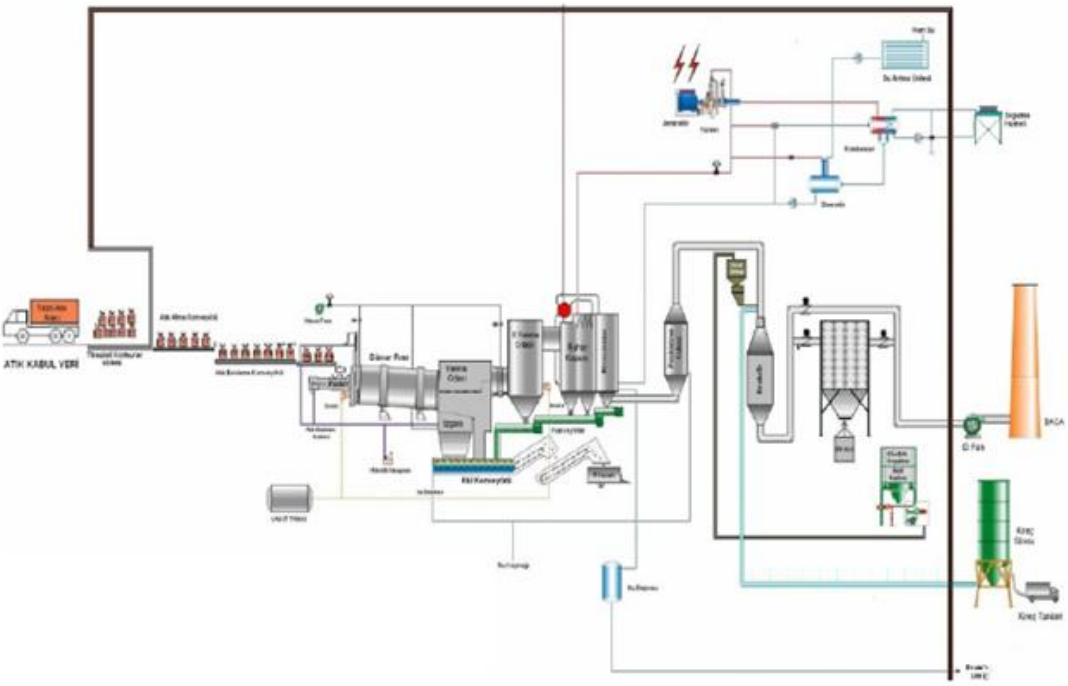

Figure 1.18 ISTAC Co. Ltd. Medical Waste Incineration Plant Flow

GENERAL
Oven Capacity : 1,0 ton/hour (3500 kcal/kg)
Waste Calorific Value to be Incinerated
Min : 2000 kcal/kg
Max : 4540 kcal/kg
Thermal Capacity of the Plant : 3.500.000 kcal/hour

THE OVEN
Type : Rotating Oven
Rotational Speed : 0-12 cycle/hour
Volume of The Oven : 27,5 m^3
Length of The Oven : 7,5 m
Diameter of The Oven : 2,73 m
Weight of The Oven : 14 tons

FLUE GAS CLEANING UNIT
1. Water Spray Tower
Tower Height : 8 m
Diameter of Tower : 2,2 m
Flue Gas Flow Rate : 10890 Nm^3/hour
Flue Gas Inlet Temperature : 170°C
Flue Gas Outlet Temperature : 140°C

2. Reactor

Compound Used : Hydrated Lime
Gas Flow Rate : 10890 Nm^3/hour
Reactor Height : 7,5 m
Reactor Width : 1,6 * 1,6 m
Lime Dosage : 10-200 kg/hour

3. Fitration Unit

Filter Type : Pulse Jet III Bag Filter
Filter Quantity : 210 pieces
Total Filter Surface : 337 m^2

FLUE : 50 m
Flue Height : 0,60 m
Flue Diameter : 14000 Nm^3/hour
Flow Rate of Flue Fan : 534 mmSS (ISTAC Co. Ltd., 2004)

CHAPTER 2

HEAVY METALS

2. HEAVY METALS

From the funnels of waste incineration plants heavy metals including lead and cadmium are released. Most of the heavy metals have long life and their impact on health is extremely bad. As the result of improvements in air pollution prevention equipment technologies, recently a decrease in amount of heavy metals released from waste incineration funnels is observed. Against all these, heavy metals are released from new facilities and these are added to the already existing amounts in the environment and piles up on men and the environment. Like in dioxins, as the result of the fight made with air pollution prevention equipments, heavy metals that do not vent into the atmosphere will accumulate in facility ashes and finally air pollution will be created as these ashes are transferred to storage sites. Mercury causes blindness, muscle deformation, birth deformation and death. Arsenic is carcinogenic and irritates respiratory tract. Cadmium is carcinogenic and causes cardiovascular diseases and is extremely toxic for the aqua life. Chromium is formed with six-valence in excess air and three-valence in starved air. Six-valence-chromium is carcinogenic and causes respiratory tract diseases and skin damages, but no significant damage of three-valence chromium is seen on life. They are checked like particle materials. However if a specific amount of six-valence chromium is found in ash, extra process is necessary to transform this into three-valence form (Y., 2002)

2.1. DIFFUSION OF HEAVY METALS

Heavy metals are classified as vital and non-vital according to their rate of participation in biological processes. The ones defined as vital must be available in the structure of the organism at a specific concentration and these metals need to be consumed by food regularly as they participate in biological reactions. For example copper is an indispensable part of red blood cells in animals and human and part of the oxidation and reduction process (Davutoğlu, 2004).

The most important industrial activities effective in environmental distribution of heavy metals are;

Cement production,

- Iron and steel industry,
- Thermal power plants,
- Glass production,
- Metal industry,
- Waste and waste sludge incineration facilities (Öztürk H. İ., June 2009).

2.2. TOXIC EFFECT OF HEAVY METALS

Waste water arising from various industrial activities contains metals either in trace quantities or in high concentrations. Metals may create toxic effects on the living creatures in the disposal environment based on their concentration. Elements having aqua concentrations of ppm (mg/L) or lower, for example ppb (µg/L) are known as trace elements. Concentration of most pollutant is at this level. Among these metals which can be unfavorable even in trace quantities, the most important group is cadmium, lead, copper, chromium, zinc, manganese, mercury, arsenic, antimony, nickel, selenium, molybdenum which we refer to as heavy metals. Some of these support life where as some of them can be considered as toxic (Güçlü, 1999).

Heavy metals in water are found in very small quantities. All of these are toxic to aquatic organisms. Most of them are fatal on border of 1 ppm. Toxic effects of heavy metals are given in Table 1.9 (Yıldız S., 2004)

Table 2.1 Impact of Heavy Metal Ions on Human Health (Derrell, 1991; Brohi, 1998)

Pb	Gum turning to blue, anemia, muscle lock, stroke, mind disorder, cerebral hemorrhage, nervous system diseases
Cu	Stomach ache, vomiting, bleeding, asthenia, anemia, jaundice, breathing difficulty, leukocytosis
Mn	Digestion disorder, nephrosis and heart disorders are seen in acute intoxication. Stored in lungs and brain.
Cd	Suprarenal gland effects, anemia, reduced hemoglobin levels
As	Arsenic is taken by respiratory, digestive system and skin. It is stored in hair, nails, liver and kidneys. It has carcinogenic effect.
Co	Cobalt toxicity is a rare event. Cobalt concentration reaches up to 3000 times the cobalt level.
Cr	Skin lesions, ulcer, cancer, digestion scars, respiratory tract damages
Ni	Extreme dosages can cause cancer

2.2.1. Lead (Pb)

Water hardness decreases the toxic impact of lead. For example water containing 50 mg L-1 calcium eliminates the toxic impact of 1.0 mg L-1 lead (Brown, 1971).

Various food studs contain different amounts of lead. According to researches made lead particles of 01.-0.3 µm can be absorbed 27-62 % according to type of the lead compounds, its respiration rate and depth (Sımkıss, 1981). Rate of excretion of absorbed lead is very slow and accumulates in the body throughout the life of the person (Sımkıss, 1981) (Yalçın M., 1997).

2.2.2. Chromium (Cr)

Chromium is extremely used in technique. Chromium is used in the industry; chemical and paint industry, leather production, glass industry, textile painting, photograph industry, production of non-corrosive alloys and production of varnish and ink in small amounts (Yıldız S., 2004).

Chromium is available almost in all tissues of the human body. Acceptable level of daily chromium intake from food is around 50-200 µg/day (RDAS National Research Council, 1989).

2.2.3. Cobalt (Co)

Natural concentration of cobalt is 0.3-0.7 mg/l. 10 mg/l concentration creates toxic effect for living creatures. However it is possible that this value is not used as a full limit (Uzunoğlu, 1999).

Cobalt is used in production of alloys, paints, varnishes and ink. Cobalt is special element for some human and animals. The reason for this arises from including of this in the structure of vitamin B12 (Yıldız S., 2004).

2.2.4. Nickel (Ni)

10-50 mg nickel in 1000 g of soil is acceptable (Sehmel, 1962). In general nickel is used with chromium in chromium coating of some motor vehicles. It is determined that 0.001 mg m-3 of nickel enters into one of the lungs by respiration; it may lead to cancer (Şen, 1993; H., 1980).

2.2.5. Cadmium (Cd)

Cadmium is a soft and silver white metal that is quiet electropositive and that can be processed (Perkins, 1984).

Cadmium intoxication causes liver damages, renal failure and lung diseases. The reason for this intoxication is that cadmium passes in enzymes instead of zinc. As the rate of zinc use increases, intoxication arising from cadmium inside the zinc increases as well (Stoker, 1972).

2.2.6. Manganese (Mn)

Manganese is the least toxic metal among heavy metals (Uzunoğlu, 1999).

Atom number of manganese is 25 and it is discovered in 1774. It has grayish metal color. It is not available in pure metal form in nature. There are more than 300 minerals in nature that contains manganese and elements containing minimum 35% of manganese are referred to as “manganese ore” Important minerals are pyrolusite (MnO_2), psilomelane ($BaMn_9O_{18}.2H_2O$) Manganite ($Mn_2O_3.H_2O$), Braunite ($3Mn_2O_3 MnSiO_3$), Rhodochoriste ($MnCO_3$), Hausmanite ($MnMn_2O_4$). (ATSDR; Jeoloji Mühendisleri Odası)

Manganese is an important mineral for human body. It needs to be consumed every day in specific amounts. However high amounts of manganese consumption create toxic effects on body. Effects of manganese are mainly observed in respiratory system and brain. Symptoms of manganese intoxication are hallucinations, dysmnesia and nervous diseases. Manganese may at the same time cause Parkinson, pulmonary embolism and bronchitis (Öztürk H. İ., June 2009).

2.3. ADSORPTION OF HEAVY METALS

Metals are adsorbed to the surfaces of clay minerals inside the ground by cation exchange capacity. Metals are tightly bonded to clays and organics in general. Processes between metal and clay depend on factors like metal type, ground type, pH and temperature. The progress of metal concentration in the ground having low cation exchange capacity can be clearly observed. By adjusting the ground pH, in grounds with low cation exchange capacity, progress of metals inside the ground can be stopped (Braja, 1990).

Adsorption of metal ions in aqua solutions over metal oxides and clay minerals is an interesting and important issue in analytic and environment chemistry research field. Today important environmental events take place in many countries regarding heavy metal and radionuclide pollution. Adsorption appears to be an important process in demonstrating, observing these events and finding solutions (Stumm, 1996).

2.3.1. Adsorption

It is defined as increase of accumulation and concentration of a material on a surface or cross section. This process can take place in cross section of two different phases (Yıldız S., 2004).

Adsorbent is the surface element adsorbed to the element kept on surface. Solid-liquid adsorption plays an important role in drinking water and waste water treatment. For adsorption techniques in water treatment, various chemical materials are used. Zeolite, active carbon, natural and artificial adsorbents are used to retain heavy metals in waste water (Şengül, 1997).

Adsorption is referred to as the change in concentration at the limit surface of a solid or liquid. Increase of concentration will be referred to as positive adsorption and decrease will be referred to as negative adsorption. Material on the surface with higher concentration will be referred to as adsorbent or adsorber (Şeren, 2000).

Adsorption is increase of pollutant accumulation and concentration on surface or surface cross section. Adsorption in water and waste water treatment is realized between a liquid and solid. The material kept on surface is referred to as adsorbed material or adsorbate and the material keeping it on surface is the adsorbent (Yılmaz N. , 2007).

Second effective force for adsorption is the tendency of liquid to solid. Adsorption types are determined based on these two forces. Factors effective for determining these types are the electrical attraction of liquid to adsorbent, Van der Walls attraction and chemical structure. These are in successive orders transformation adsorption, physical, chemical and biological adsorption (Tsezos, 1981).

Adsorption process takes place in the cross section of two different phases like liquid-liquid, gas-liquid, gas-solid, and liquid-solid. During adsorption process, the material kept on surface is called adsorbate and the material holding it is called as adsorbent (Weber, 1972).

2.3.1.1. Transformation Adsorption

Transformation adsorption is the adsorption based on first type ion transformation. Transformation adsorption is accumulation of ions of a material as the result of electrostatic attraction towards loaded areas on surface. For two potential ionic adsorbate at the same concentration, ion load will be the indicative factor for transformation adsorption. Accordingly in an environment where there is one and three-valence ions, three-valence ion will be attracted to the adsorbent surface more strongly (Şencan, 2001).

2.3.1.2. Physical Adsorption

Physical adsorption is characterized with low adsorption heat and balance is easily established. Many pollutants and gas in water and waste water is absorbed on active carbon physically. In such an adsorption, the force that causes gases to deviate from ideal form and to turn into liquid is considered to be the same type of force like Van der Walls (Yılmaz N., 2007).

Amount of adsorption decreases rapidly as temperature increases or as it goes a little above critical temperature of the adsorbed compound. As physical adsorption is reversible, molecule adsorbed detaches from the surface when concentration decreases (Şencan, 2001).

2.3.1.3. Chemical Adsorption

Chemical adsorption is also referred to as "activated adsorption" (Tsezos, 1981) (Şencan, 2001).

In chemical adsorption, a chemical bond is formed between adsorbent and adsorbate. This is generally a covalent bond. Adsorption is single layered and when active points that molecules will bond to on the surface ends, adsorption stops (Yılmaz N., 2007).

Chemical adsorption is specific and is realized by forces that are stronger than physical adsorption. Chemical adsorption is not reversible in general (Yılmaz N., 2007).

Table 2.2 Chemical adsorption rate is lower compared to physical adsorption

Parameter	**Physical Adsorption**	**Chemical Adsorption**
Adsorbent	All solid materials	Some solid materials
Adsorbed	Gases that are under critical temperature, liquids, dissolved solids	Some chemical reactive substances, dissolved solids
Temperature	Low temperature	High temperature
Adsorption Temperature	Low	High
Velocity	High Velocity	Vary depending on temperature
Desorption	High recycling	No recycling
Bond forces	Between Molecules	In Molecules

Enthalpy effect	Always order of exothermic condensation	Often the order of the temperature of exothermic reaction
Importance	for the determination of surface area and pore size	Expression of surface-reaction kinetics and active

2.3.1.4. Biological Adsorption

Biosorption term means specific number of processes carried out at the cell wall independent from the metabolism mainly instead of oxidation by aerobic or anaerobic metabolism (physical and chemical adsorption, electrostatic interaction, complexing, ion exchange and micro scaling) (Yılmaz N., 2007).

2.3.2. Factors That Effect Adsorption

2.3.2.1. Surface Area

Adsorption is a surface event. For this reason maximum adsorption amount is directly proportional with specific surface area (Yılmaz N. , 2007).

Accordingly adsorption amount increases with the unit surface weight of solid adsorbent, in other words if it is well separated and has multiple pores. As it is not easy to determine the surface area of the adsorbent, amount of material adsorbed per unit weight of the adsorbent is taken. As the surface area of the adsorbent increases, amount adsorbed will increase (Şencan, 2001).

2.3.2.2. Particle Size

Size of carbon particle effects adsorption rate. Adsorption rate increases as the size of the particle decreases. Adsorption speed and rate of particles in fixed sizes changes linear to the dosage of an adsorbent at a specific dosage range. This dosage does not create major changes in the purity concentration at the solution phase (Yılmaz N., 2007).

2.3.2.3. Size of the Molecule of the Adsorbed Material (Adsorbate)

As it enters inside the pores of a carbon particle to adsorb molecules, molecular size plays an important role in adsorption (Yılmaz N., 2007).

For materials with porous structure like active carbon, converting large particles to small particles creates small pores suitable for adsorption in carbon. Accordingly carbon becomes suitable for adsorption (Yılmaz N., 2007).

2.3.2.4. Solubility of Adsorbed Material

One of the most important factors of adsorption is the solubility of the adsorbate that controls the balance of adsorption. Generally there is a reverse correlation between the adsorption amount of a material and the solubility in the environment where adsorption of this material took place (Yıldız S., 2004).

2.3.2.5. pH Value of the Media

pH value of the environment adsorption took place has impact on adsorption amount for one or more reasons. As hydrogen (H+) and hydroxyl (OH-) ions are adsorbed strongly, adsorption of other ions is affected from the pH of the solution. Ionization of acidic or basic compound affects its adsorption and even though it does not control the ionization level at pH, it has impact on adsorption (Yılmaz N., 2007).

Generally adsorption of organic pollutants increases with decreasing pH (Şencan, 2001).

2.3.2.6. Temperature

In many reactions generally it is said that when temperature increases, reaction speed increases. In adsorption process, temperature is an important criterion and characterizes adsorption type and is effective mainly on adsorption speed (Şencan, 2001).

As adsorption reactions are exothermic reactions, adsorption rate increases as temperature decreases (Yılmaz N., 2007).

2.3.2.7. Contact Time

Finding the optimum contact time for the adsorbent and adsorbate used in adsorption method is important especially in treatment of industrial waste water that has this adsorbate characteristic (Bayrak, 2006)

2.3.3. Adsorbents

2.3.3.1. Zeolite

Zeolites are group of naturally occuring crystaline, hydrated alumina-silicates and contain exchangeable alkaline and alkaline-earth cations. Zeolites have many useful characteristics. They can be used in different applications such as ion exchange, filtering, odor removal, chemical sieve and gas adsorption. The regular void spaces in their lattice allow molecular sieving and selective separation based on size and charge. The porosity creates a large effective surface area for adsorption (Aydın, 2007).

Table 2.3 Composition and adsorption capacity of some zeolites

Zeolite	The Composition	The largest windows size (nm)	The biggest molecule adsorbed
A	$Na.AlO_2.2.H_2O$	0,42	C_2H_4
X	$Na.AlO_2.I.3SiO_2\ 3H_2O$	0,74	$(C_2H_9)_3N$
Analcime	$Na.AlO_2.2SiO_2\ H_2O$	0,26	NH_3
Mordenite	$Na.AlO_2.5SiO_2\ 3H_2O$	0,67x0,70	C_2H_4
Chabazite	$2Ca.4AlO_2.8SiO_2\ 13H_2O$	0,31x0,44	n-paraffin
L	$Na/K.AlO_2.3SiO_2\ 2.5H_2O$	0,71	$(C_2H_9)_3N$
Clinoptilolite	$Na/K.AlO_2.5SiO_2\ 4H_2O$		O_2
Erionite	$Ca/Mg/2Na/2K.2AlO_2.6SiO_2\ 6H_2O$	0,36x0,52	n-paraffin
Faujasite	$Na.Ca.Mg.5AlO_2.11SiO_2\ 19.6H_2O$	0,74	$(C_2F_3)_3N$
Offrerite	$2,5(Mg/Ca/2K).5AlO_2.13SiO_2\ 15H_2O$		Cyclohexane
Plillipsite	$K/Na.AlO_2.2SiO_2\ 2H_2O$		H_2O

There are 40 types of natural zeolite and also more than 150 artificial zeolites in nature. The mostly available zeolite minerals in nature are analcime, philippsite, sabazite, heulandites, leumontite, natrolite, stilbite, erionite, clinoptilolite, epistilbite, faujasite, ferrierite, gismondine, gonardit, harmotom, mordenite, scolesite, stilbite, thomsonite, warakit and yogovaralit (Hay, 1978).

2.3.3.1.1. Areas of Use of Zeolite

Use of zeolites as building materials in the form of volcanic ashes exposed to alteration goes beyond 2000 years. During the historical development, with participation of zeolite types with different features, the trend of using natural zeolites in many countries for building materials continue (Kurama, 1994).

- A - Purification
    - I - Drying
        - Natural Gas (LNG content)
        - Fragmented Gas (Ethylene Plant)
        - Insulating Glass
        - Cooler
    - II - CO_2 Removal
        - Natural Gas
        - Cryogenic Air Separation Plant
    - III - Removal of Sulphure Compounds
        - Cleaning of Natural Gas and Liquefied Petro Gas
    - IV - Pollution Prevention
        - Removal of $HgNO_2.SO_4$
- B - Bulk Separation
    - I - Regular / Isoparafin Separation
    - II - Xylene Separation
    - III - Olefin Separation
    - IV - O_2 Separation from Air
    - V - Sugar Refining

Table 2.4 Adsorption / ion exchange applications of Zeolites (Kurama, 1994)

Bulk Applications	Adsorption / Ion Exchange Applications
Filler Paper	* Oxygen And Hydrogen Separation In Air
Pozzolinik Cement And Aggregate	- Oxygen Production
Building Block	- Coal Gasification
Light Weight Aggregate	- Flue Gas Cleaning (NO_x, SO_2, CO_2)
Fertilizer And Soil Conditioner	* Acid-Resistant Adsorbent In Drying And Purification Processes
Animal Feed Additive	- Natural Gas Purification
Antibiotic Material And Toothpaste Additive	- Production Of Petroleum Products
Ceramic Material Additive	* Foul Odor Removal
	* Moisture Content Control, Moisture Absorbing Material

	* Solar Energy Collection
	* Natural Gas Carrier Material
	* Ion Exchange Applications
	- Radioactive Waste Separation
	- Removal Of Used Water And Wastes
	- Aquaculture
	* Search For Mineral Deposits
	* Metallurgy
	* Cleaning Oil Spills

2.3.3.1.2. Impact of Zeolite on Decontamination

In zeolites, adsorption is filling the micro pores instead of being adsorbed on surface. The reason for this is that the amount of molecule that is attached to the exterior surface of zeolite crystal is generally one percent of the amount of molecules that enters into and fills the spaces inside the crystal structure (Çalış, 2003).

Area of micro pores that control adsorption process is a couple of hundred m2/g. Zeolites can adsorb gas or liquid molecules up to 30% of their dry weights (İnan, 2002).

There are several studies reporting adsorption of heavy metals by zeolites. Thesestudies generally report the comparisons of the adsorption characteristics of zeolite against some heavy metals as a function of mineralogy, testing conditions (pH, slurry concentration, heavymetal concentration, temperature, and grain size), type of heavy metals, etc. (Ören, 2007)

For example, Zamzow & Murphy (Zamzow, 1992) investigated the removal capacity of a wide variety of zeolite minerals against lead ions. The result of this study showed that lead removal capacity of minerals is in the orders of: phillipsite > chabazite > erionite > clinoptilolite > mordenite. Zamzow & Murphy (Zamzow, 1992) enlarged this study for the various heavy metals such as cadmium, copper and zinc. The results indicated that clinoptilolite and mordenite have the lowest adsorption capacities among other minerals against tested heavy metals.

Clays or zeolites are widely used for removing hazardous leachates from industrial wastewater. Moreover, zeolites can be used as permeable barriers in order to remove heavy metals on account of negatively charged surface (Jacobs, 1999) (Czurda, 2002).

Mondale et al. (1995) conducted batch and column experiments with different types of natural and sedimentary zeolites and stated that the increasing order of adsorption capacity in terms of mineralogy is as follows: erionite > chabazite > clinoptilolite > mordenite. It is also given that cation selectivity during the experiments by the zeolite minerals is: $Ag+ > Pb_2+ > Cd_2+ > Zn_2+ \geq Cu_2+ >> Ni_2+ > Hg_2+$ (Mondale, 1995)

2.3.3.2. Bentonite

Bentonite is smectic group clay mineral and contains more than 85% montmorillonit and has three layer structures. Various physical and chemical features of clay minerals like its plastic features, absorption skills, anion and cation migration capacities, low pore level allows them to be used in different areas (Şeren, 2000).

Clays which are other elements of the smectic group that is derived from montmorillonite with main mineral or isomorphic ion transformation of montmorillonite is generally named as “bentonite”. Sodium bentonite (Na-B) whose main mineral is Na-montmorillonit (Yalçın M., 1997).

Bentonite is colloidal aluminum hydro silicate and its volume increases between 10 to 30 times with water. This swelling function is caused by hydrophyles. Until bentonite temperature goes above 200° C swelling function is maintained and above 600 °C, swelling function is completely lost (Yalçın M., 1997).

In the treatment processes based on adsorption method, use of bentonites is suitable contrary to their low adsorption capacities (Şeren, 2000).

2.3.3.2.1. Areas of Use of Bentonite

In the paper industry, bentonites are used in many industries like production of ceramics used for different purposes, bleaching of vegetable oil, beer, wine and fruit juices, treatment of radioactive wastes, waste waters, production of pharmaceuticals, perfume, soap, detergent, rubber, plastic (Öner, 1999).

Bentonites are used in oil and water based paints. It is possible to talk about their thickener and dispersible effects and emulsifier impact (Şeren, 2000).

Also chemical additives added to latex (raw material of rubber) can be used for thickening and stabilizations. Rubber based paint and adhesives can also be used as emulsion stabilizers (Hauser, 1955).

2.3.3.2.2. Impact of Bentonite in Decontamination

Various cations in soil are retained especially on the surface of the clay particles in a way that it will be possible to change place with other cations. This is referred to as cation adsorption. The power of clay particles to adsorb cations changes according to the following:

- Electrical loads of colloidal particles
- Type of clay
- Type of clay adsorbed (Şeren, 2000)

Cation adsorption arises from electronegative loads that clays have. These negative loads draw on them the positive loaded cations and water molecules in the solution according to coulomb law. So cation is kept on the surface of the clay particle (Şeren, 2000).

2.3.4. S/S (Stabilization/Solidification)

Stabilization and solidification (S/S) is a treatment option applied before storage for different types of industrial wastes. This is especially suitable for hazardous wastes that contain heavy metals (Malviya, 2006).

As legal restrictions on storage increase, S/S technology will play an important role in turning wastes suitable for storage conditions. Low permeability and low pollutant leakage achieved after S/S will enable wastes which are not allowed for storage to be accepted to domestic waste storage areas (Yılmaz O. Ü., 2003).

It is known that the most efficient application of S/S technology is in the treatment of hazardous wastes that contain toxic metals. There are many published researches regarding S/S of wastes that contain chemicals and metals. S/S technology tries to bond heavy metals to solids resistant to leakages by using bonding agents like volatile ashes and lime (Yılmaz O. Ü., 2003).

In stabilization, bonding materials like volatile ash, cement kiln dust, high kiln clinker, various clays etc. are used along with the cement (Conner, 1990).

In S/S systems, 3 basic bonding mechanisms are seen: a) precipitation, b) adsorption to mineral surface and c) participation in cement hydration products (Glasser, 2006).

S/S is known as a method that limits actions and solubility of pollutants by mixing them with various bonding materials. Bonding materials used in S/S change the pH level of the waste and decrease especially the solubility of heavy metal pollutants. Metals are not decomposed or altered by chemical or thermal methods. In order to prevent them from being released to environment again, they must be transformed into the most non-soluble form possible. Stabilization tries to treat the waste by lowering the pH level to the point when metal solubility of some metals is at minimum (Conner, 1990).

CHAPTER 3

LEACHATE

3. LEACHATE

The liquid formed by degradation of organic compounds in solid waste storage areas are called “leachate” Leachate are waters that are dissolved and suspended which contain physical, chemical and biological contamination. Leachate is composed of complex mixture of organic and inorganic compounds that have a unique odor (Aydın, 2007).

3.1. FORMATION AND AMOUNT OF LEACHATE

Leachate contains many chemical materials most of which are dissolved. In the storage environment where many chemical biological reaction took place, as rain water and water arising from dissolution are filtered, organic and inorganic compounds are washed and mix with leachates (Aydın, 2007).

The most basic process in leachate formation is transfer to water of compounds that can directly dissolve in water.

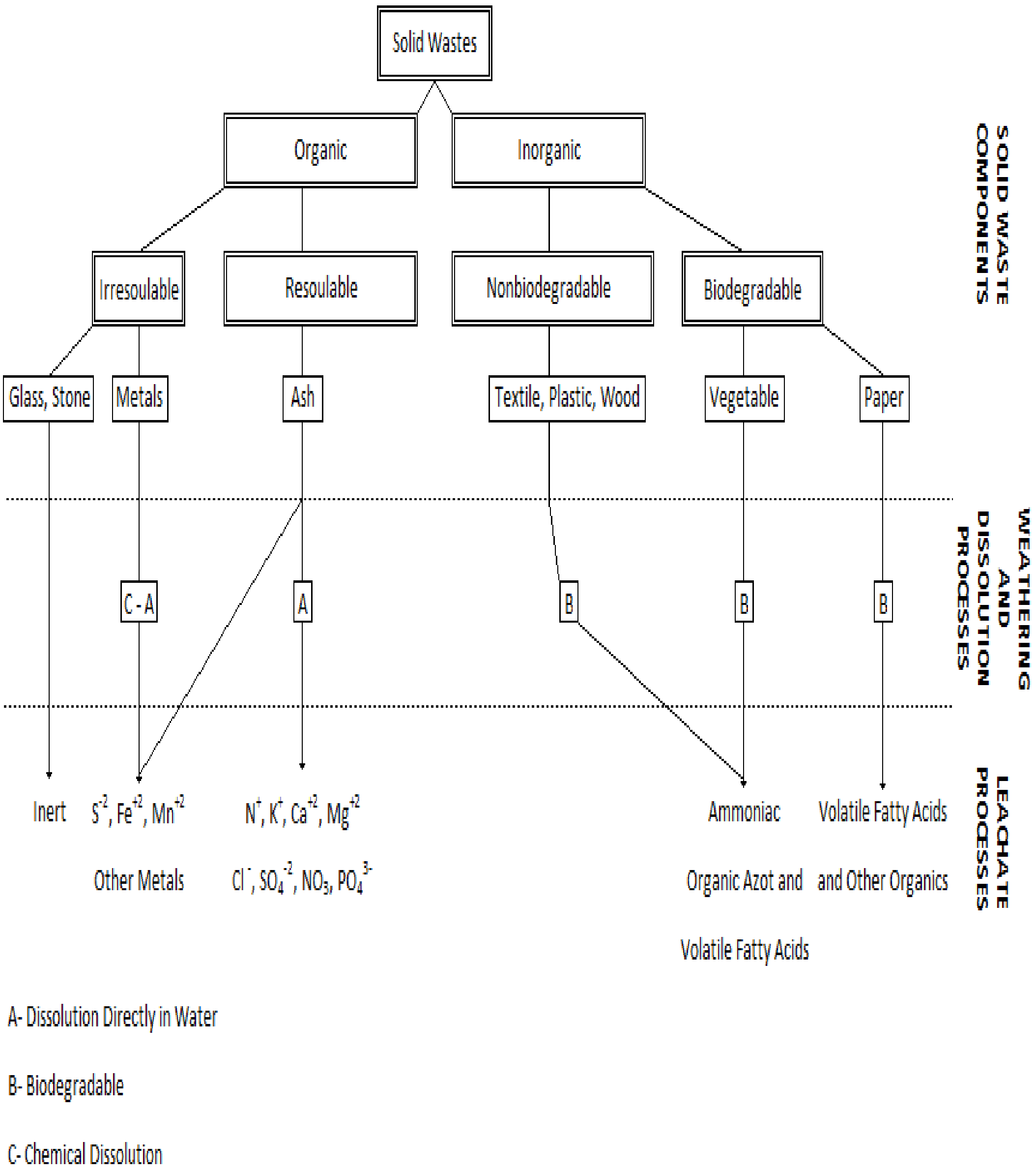

Figure 3.1 Components of Solid Waste and Composition of Leachate (Orkun, 2007)

Factors that are effective on leachate formation;

- Climate conditions and hydro geological features: Rain, melting of snow, leakage of underground water

- Processes carried out on site and operating conditions: Waste pre-treatment, compression, flora, top layer soil and plastic membranes, side walls, irrigation, leachate recycling

- Waste features: Permeability, waste age, size of the particle, density, initial humidity content

- Internal processes: Settlement of waste, organic material decomposition, gas-heat production and transfer (Özgeçmen, 2007).

Leachate amount changes according to;

- Waste type,
- Storage style and form,
- Topography,
- Top layer soil features,
- Flora on top layer soil,
- Waste collection methods,
- Compression equipments used at storage site (Özgeçmen, 2007).

Age of the storage site and solid wastes decomposition phase are the most important parameters that effect leachate compounds. Strategy of controlling leachate can be examined under four groups;

1. Volume control,
2. Composition control,
3. Purification,
4. Final disposal (Aydın, 2007)

3.2. LEACHATE FEATURES

Change in biodegradability of leachate is observed with BOİ/KOİ rate. At the initial phase, this rate is 0.5 or higher. Ranges between 0.4-0.6 shows that it will easily decompose the organic material in leachate. In developed landfill areas this BOİ/KOİ value is in the range of 0.05-0.2. The reason for this is that developed landfill areas contain humic and fulvic acids that do not easily decompose as biologically (Tchobanogulous, 1993).

Leachate features;

- Solid waste compounds,
- Age of the storage,
- Hydro-geological status of the storage site,
- Physical, chemical and biological activities in the storage,
- Water amount in solid wastes,
- Temperature,
- pH,
- Redox potential,
- Stabilization degree,
- Solid waste storage height,
- Operating the storage site,
- Change according to climate conditions.

The most important one of these is the waste compound. Biological, chemical and physical processes of organic and inorganic compounds generally determine the leachate characteristic (Aydın, 2007).

3.3. LEACHATE TREATMENT

In solid waste regular storage sites, leachates that arise are very hard to treat waste waters due to their high levels of organic and inorganic pollutants (Özgeçmen, 2007).

Leachate faces various problems in treatment due to their complex structure (Qasim, 1994).

These are;

- High pollutant load required selecting suitable treatment methods,
- Leachate characteristic depends on hydrologic and climate conditions based on season,
- Fluctuations in leachate amount and quality in short and long terms must be taken into consideration by the treatment facility design.

Methods used in treatment of leachate;

* Biological Treatment Methods,

* Aerobic Treatment

    * Active Sludge System

    * Lagoons with ventilation

    * Rotating bio-discs and dripping filters

* Anaerobic Treatment

    * Air-free sludge bedding Processes

    * Treatment with recycling using the body as reactor on site

* Physical-chemical Treatment Methods

* Coagulation – Flocculation – Precipitation

* Chemical Oxidation

* Ion Exchange

* Adsorption

* Membrane Filter Method

* Vaporization and Drying

* Ammonia abrasion by air

* Breaking point chlorination (Aydın, 2007)

3.4. LEACHATE TREATMENT TECHNOLOGIES OR PROCESSES USED IN LEACHATE TREATMENT

Leachate treatment requires using a series of treatment processes in order to accomplish the level of treatment. There are many studies carried out in this regard as published in literatures. However due to different pollutants they contain, leachate that may arise in every storage site should be evaluated individually and current features of leachates should be studied in detail before developing any control or management technique (Keser, 2008).

Methods developed for treatment of leachate are physical, chemical, biological and advanced treatment methods. It is hard to achieve high rate of treatment efficiency and output water quality using any of these methods individually. For this reason when treating leachates, in general combination of physical, chemical and biological methods are used and adsorption and membrane technologies are used in treatment methods (Amokrane, 1997; Bohdziewicz, 2001; Marttinen, 2002; Vogelpohl, 1995).

The efficiencies of some processes used in treatment of leachate on the removal of parameters that make up leachate characterization are given in Table 3.1. (Yıldız Ş., 2000)

Table 3.1 The Effects of Processes Used in Leachate Treatment (Yıldız Ş., 2000)

PROCESSES	**BON, mg/l**	**KON, mg/l**	**Tot.N, mg/l**	**NH_4-N, mg/l**	**Heavy Metals**	**AOX mg/l**	**Fish Toxicity**
Biological Treatment	*	* 2	*	*	+	+	7
Adsorption		* 3	+	+		*	7
Flotation	+	+	+	+	+	+	7
Fast / Slow Mixing		* 3	+	+	* 5	*	7
Filtration	+	+	+	+	+	+	7
Reverse Osmos	* 1	* 1	*	*	*	* 1	7
Membrane Bioreactors	* 1	* 1	*	*	*	* 1	7
Airing	+	+		*	+	+ 6	7
Chemical Oxidation		*	+	+	+	* 4	7
Evaporation		* 4	*	+	*	*	7
Incineration	*	*	*	*	*	*	7

* Appropriate
+ Inappropriate
1 Low efficiency on removal of small molecules
2 Inert part could not be removed
3 Low efficiency on removal of decayable organics
4 Low efficiency on removal of volatile organics
5 Not in same efficiency for every heavy metal
6 Low efficiency on removal of low volatile organics
7 Uncertain suitability

CHAPTER 4

MATERIALS AND METHOD

4. MATERIAL AND METHOD

4.1. MATERIALS

Heavy metal containing bottom ashes delivered from ISTAÇ Medical Waste Incineration Facility is used in the study. These ashes are mixed with adsorbents in different amounts for metal elimination. Bentonite clay and clinoptilolite is used as adsorbent.

Metal analysis is carried out with ICP-OES device of Turkish Atomic Energy Authority (TAEK).

4.1.1. Features of the Adsorbents Used in Experimental Study

4.1.1.1. Bentonite

Bentonite clay used as adsorbent is supplied from Çankırı, Ankara road Ballıca region by Buyruk Madencilik. Particle diameter is 1mm. As the particle diameter decreases, surface area increases, that’s why this diameter is preferred.

Figure 4.1 Bentonite

Chemical formula of the bentonite, which is a type of clay is (Na,Ca) (AI, Mg)6(Si4O10)3(OH)6.nH2O and weight of this formula as percentage shows the amount of Montmorillonit in bentonite produced. Its color can be white, gray, green, yellow, pink, purple and red. Its density is 2,6gr/cm3 and ionization capacity is extremely high.

It is separated into three (3) groups according to its chemical features (Türkmenoglu and Aker, 1990).

1- **Sodium Bentonite**: It is a bentonite that can swell up to 5-10 times when in contact with water and it is used mainly in drilling industry, casting industry and construction industry.

2- **Calcium Bentonite**: In case of contact with water it can swell up to 2-3 times of its original size and is used as clarification tool with its own sand.

3- **Sodium-Calcium (Intermediate type) Bentonite**: It is used as sodium bentonite as the result of chemical activation.

4.1.1.2. Zeolite

As an adsorption agent, natural zeolites (clinoptilolite) supplied from Balıkesir-Bigadiç region by OR-TAR Organik Tarım Ürünleri San. Tic. Ltd. Şti. is used. Zeolite particle diameter is 1mm. As the particle size decreases surface area increases and that's the reason why this diameter is preferred.

Figure 4.2 Zeolite

Table 4.1 Chemical compositions of tested materials (Ören, 2007)

Materials	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O
	(%)	(%)	(%)	(%)	(%)	(%)	(%)
Bentonite	47.28	10.97	1.28	6.81	7.90	2.81	0.22
Bigadiç Zeolite	65,85	11.22	1.09	1.07	2.94	0.49	3.05
Gördes Zeolite	63.74	11.80	1.66	1.18	1.86	0.51	2.46

4.2. METHOD USED

Ashes are mixed with adsorbents in different rates. Ash- adsorbent rate is calculated separately. Mixtures prepared are placed in columns. The purpose here was to eliminate the heavy metals that ashes contain via adsorption method. Ultra pure water is pumped into these columns with peristaltic pump. In order for all metals to enter in water, it is kept for 24 hours.

Figure 4.3 Pure Ash

Figure 4.4 Column Cell

Figure 4.5 Parts of the Column Cell

4.3. DEVICES USED

4.3.1. Induction Combined Plasma (ICP)

Metal analyses are carried out with ICP-OES device of Turkish Atomic Energy Authority (TAEK).

Figure4.6 Induction Combined Plasma (ICP)

ICP is the plasma technique at high levels like 7000-8000 K that are supported with magnetic field, where elements in the sample are turned into atoms and simulated. Plasma is referred to as ion flow in gas form. In ICP technique as plasma argon has is both inert and can be easily ionized, it is created by interacting it with magnetic area created by radiofrequency generator (Yıldız S., 2004).

Inductive combined plasma spectroscopy has high sensitivity and selectivity power thanks to plasma’s skills of atomizing and ionizing samples efficiently in trace element analysis. Assays are made with the help of radiation (ICP-AES) or isotopes (ICP-MS) used with mass and emission spectroscopy. Having sensitivity below nanogram level is a technique that is mostly required or used recently, in assay of many elements that have toxic or useful effects in biological samples (Altundağ, 2002).

With the help of sample solution, nebulizer, via plasma support gas it is brought to the quartz tube. There is the flow region inside the quartz tube which allows the sample to reach to the plasma and there is also a flow region that enables the quartz tube to cool down. On the outer part of the tube, induction reels are wrapped and reel ends are tied to a radiofrequency generator with 27 MHz-40 Mhz rate. With the current from radiofrequency generator and the current passing inside the reel, a magnetic area is created at the end of the quartz tube. In addition to this with the Tesla reels around the quartz tube, first electrodes that will form the plasmas are created (Yıldız S., 2004).

These electrons created collide with argon gas atoms by speeding up at the magnetic area at the end of the tube. By this collision, many argon ions and electrons are obtained. With continuous repeat of these processes, plasmas that have a temperature between 6000-10000 K are obtained. Sample brought under the quartz tube enter the sample and turn into atoms and stimulation occurs. Sample obtained is neutral and contains only the ions of Ar gas, electrons and sample ready for stimulation. Basic components of ICP are given in figure 1.1 (Yıldız S., 2004).

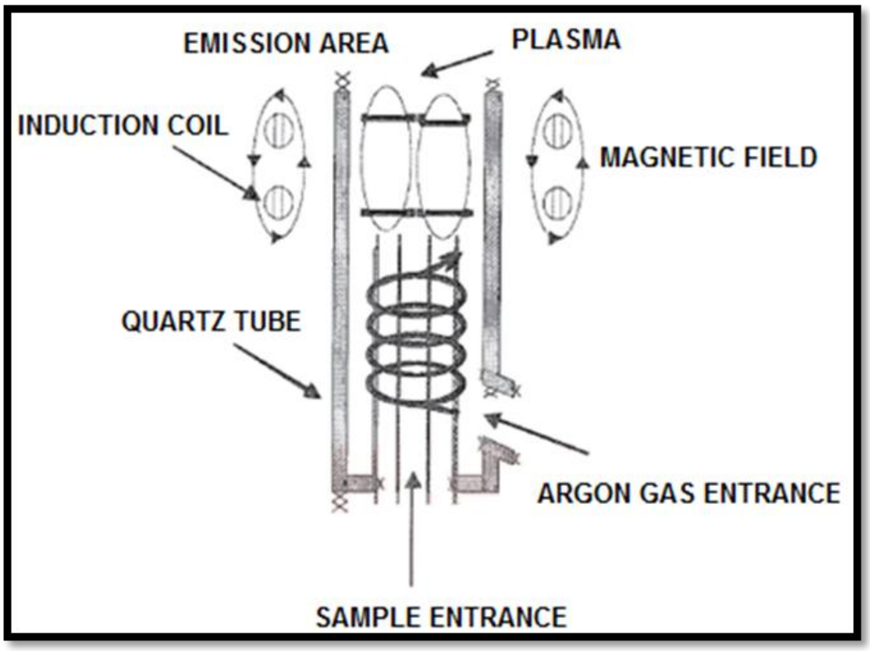

Figure 4.7 The main components of ICP

4.3.2. pH-Meter

Ultra pure water is used in the study. pH of the pure water used in all tests is taken as 7. Measurements are made in Fatih University Environment Engineering Department Environment Chemistry Laboratories with a pH meter that is ……. Brand.

Figure 4.8 ph-Meter

4.3.3. Grinder

In the study, diameter of heavy metal containing ashes delivered from ISTAÇ Medical Waste Incineration Facility is decreased to 200 micron meter with Sample Mill MRC Scientific Instruments brand grinder in Fatih University Environment Engineering Department Soil Mechanic Laboratory.

Figure 4.9 Grinder

4.3.4. Assay Balance

While trying to adjust the ash-adsorbent mixture rates in the study, weights are measured every time. For weight measurement, precise scale of Weight Zero Densi DS-1 brand is used in Fatih University Environment Engineering Department Soil Mechanic Laboratory.

Figure 4.10 Assay Balance

4.3.5. Peristaltic Pump

Ultra pure water is pumped into these columns composed of ash-adsorbent mixture with a peristaltic pump. Chrom Tech brand peristaltic pump is used in Fatih University Environment Engineering Department Soil Mechanic Laboratories.

Figure 4.11 Peristaltic Pump

4.3.6. Filter

Leachate obtained from columns composed of ash-adsorbent mixture are filtered via … brand filtration devices having filters with a diameter of 45 micron. This process is carried out in Fatih University Environment Engineering Department Environment Chemistry Laboratory.

Figure 4.12 Filter

4.4. EXPERIMENTAL SECTION

In this study experimental study shall be explained. In the study ash-adsorbent is mixed in specific rates and pumped into the column-cells. To understand adsorption capacity of adsorbents, experimental section is divided into 4. In experiment 1 ash-zeolite (clinoptilolite) mixture is adjusted in specific rates and leachate is taken from column cells and in Experiment 2, same ash –zeolite (clinoptilolite) mixtures are kept for one week and second leachate is taken. In Experiment 3, ash-bentonite mixture is adjusted in specific rates and first leachate is taken from column cells and in Experiment 4, same ash- bentonite mixture is kept for one week and second leachate is taken. Leachate taken are collected in plastic containers and kept in refrigerator of +4 c Fatih University Environment Engineering Department Soil Mechanic Laboratory for measurement purposes.

4.4.1. Experiment 1

Ash-zeolite (clinoptilolite) mixture was made in various rates. Percentage distribution of mixture rates are as follows; 10%, 15%, 20%, 25%, 30%, 40%, 50%, 60%. Total weight of the mixture in the study is taken as a constant and change in ash-zeolite (clinoptilolite) rates is calculated according to rates and these are then placed in column-cells. Column-cell is made of plexy glass with a diameter of 6cm and height of 15 cm. (Figure 4.5) Filter made of stainless steel is placed on column cell diameter. Cells made are fixed with iron studs. (Figure 4.4)

Following this phase, cells are filled with ash-zeolite (clinoptilolite) mixtures and then cells are closed. Ultra pure water is pumped into each cell formed via peristaltic pump. Water weight supplied to the cell is measured and recorded. It is kept for 24 hours to ensure that all metals pass into the water. Leachate obtained are collected in plastic containers and kept in +4 c in the refrigerator of Fatih University Environment Engineering Department Soil Mechanic Laboratory for measurement purposes.

Figure 4.4 Column Cell

Figure 4.5 Parts of the Column Cell

4.4.2. Experiment 2

Same ash-zeolite (clinoptilolite) mixture in Experiment 1 is kept for 1 week. Weight of each mixture is measured before creating the column-cell. Ultra pure water is pumped into each cell formed via peristaltic pump. Water weight supplied to the cell is measured and recorded. This way by re-forming the cells, it is tested to see whether there is any change in the adsorption capacity of the adsorbent. It is kept for 24 hours to ensure that all metals pass into the water. Second leachate obtained are collected in plastic containers and kept in +4 c in the refrigerator of Fatih University Environment Engineering Department Soil Mechanic Laboratory for measurement purposes.

Figure 4.13 Column Cell Used with Peristaltic Pump

4.4.3. Experiment 3

Ash-bentonite mixture is made in different rates. Percentage distribution in mixtures here is; 10%, 15%, 20%, 25%, 30%, 40%, 50%, 60%. In the studies carried out, total weight of the mixture is taken as constant and change in ash-bentonite amount is calculated according to rates and placed in column-cells. Column-cell is made of plexy glass with a diameter of 6cm and height of 15 cm. (Figure 4.5) Filter made of stainless steel is placed on column cell diameter. Cells made are fixed with iron studs. (Figure 4.4)

Following this phase, cells are filled with ash-bentonite mixtures and then cells are closed. Ultra pure water is pumped into each cell formed via peristaltic pump. Water weight supplied to the cell is measured and recorded. It is kept for 24 hours to ensure that all metals pass into the water. Leachate obtained are collected in plastic containers and kept in +4 c in the refrigerator of Fatih University Environment Engineering Department Soil Mechanic Laboratory for measurement purposes.

4.4.4. Experiment 4

Same ash-bentonite mixture in Experiment 3 is kept for 1 week. Weight of each mixture is measured before creating the column-cell. Ultra pure water is pumped into each cell formed via peristaltic pump. Water weight supplied to the cell is measured and recorded. This way by re-forming the cells, it is tested to see whether there is any change in the adsorption capacity of the adsorbent. It is kept for 24 hours to ensure that all metals pass into the water. Second leachate obtained are collected in plastic containers and kept in +4 c in the refrigerator of Fatih University Environment Engineering Department Soil Mechanic Laboratory for measurement purposes.

CHAPTER 5

RESULTS AND DISCUSSION

5. RESULTS AND DISCUSSION

Many experiments were made to search stabilization of both Zeolite and Bentonite. With both adsorbents, 10%, 15%, 20%, 30%, 40% and 50% mixtures were used to observe the difference occurred with the pure ash. The heavy metal amounts in pure ash are shown in Table 5.1.

Table 5.1 The Amount of Heavy Metals in Pure Ash

Heavy Metal	Amount
Cadmium	0,360 ppm
Cobalt	1,525 ppm
Crom	0,445 ppm
Manganese	11,237 ppm
Nicel	1,340 ppm
Lead	2,330 ppm

5.1. EXPERIMENT 1

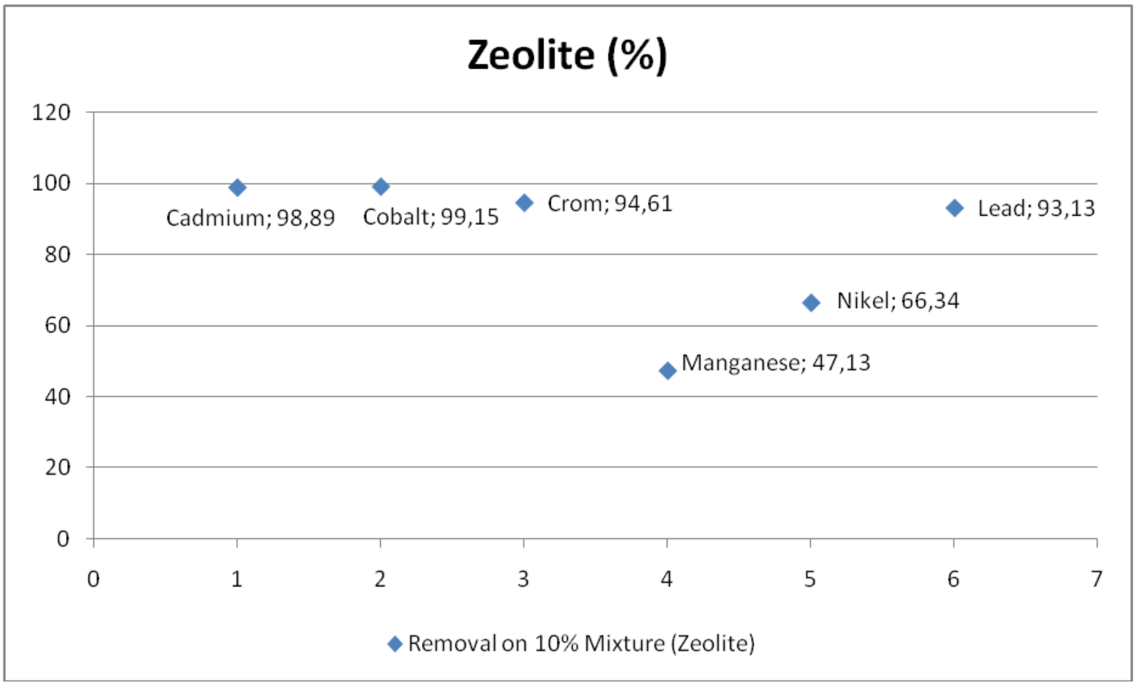

Figure 5.1 Heavy Metal Stabilization in %10 Zeolite & Pure Ash Mixture

The Cd amount in pure ash is 0.36 ppm. But the amount of Cd remains in 10% zeolite + pure ash mixture decreased to 0,004 ppm which means 98.90% stabilization. So, it can be said that zeolite is a good adsorbent at stabilization of Cd in pure ash.

The Co amount in pure ash is 1.525 ppm. But the amount of Co remains in 10% zeolite + pure ash mixture decreased to 0,013 ppm which means 99.15% stabilization. So, it is observed that zeolite is a good adsorbent at stabilization of Co in pure ash.

The Cr amount in pure ash is 0.445 ppm. But the amount of Cr remains in 10% zeolite + pure ash mixture decreased to 0,024 ppm which means 99.10% stabilization. So, it can be said that zeolite is a good adsorbent at stabilization of Cr in pure ash.

The Mn amount in pure ash is 1.237 ppm. But the amount of Mn remains in 10% zeolite + pure ash mixture decreased to 0,654 ppm which means 47.13% stabilization. We observed that zeolite have difficulties stabilizing Mn. It is estimated that the reason may be the Mn content in zeolite’s chemical structure.

The Ni amount in pure ash is 1.34 ppm. But the amount of Ni remains in 10% zeolite + pure ash mixture decreased to 0,451 ppm which means 66.34% stabilization. So, it can be said that zeolite is a good adsorbent at stabilization of Ni in pure ash.

The Pb amount in pure ash is 2.33 ppm. But the amount of Pb remains in 10% zeolite + pure ash mixture decreased to 0,16 ppm which means 93.10% stabilization. So, it can be said that zeolite is a good adsorbent at stabilization of Pb in pure ash.

Table 5.2 Stabilization of Heavy Metals with Zeolite (%)

Heavy Metal	15%	20%	30%	40%	50%
Cadmium	96,67	98,33	99,72	96,94	97,50
Cobalt	99,54	100,00	99,80	99,54	99,48
Crom	95,73	91,24	95,51	92,58	72,81
Manganese	73,73	78,82	60,23	57,07	87,47
Nicel	79,78	91,57	90,22	79,93	91,12
Lead	95,62	98,15	94,12	95,28	96,01

Although a reasonable stabilization level is observed in 10% Zeolite & Pure ash mixture, more experiments were done with different mixture levels. As in Table 5.1, the stabilization levels in mixtures other than 10% are also resulted in a good way.

5.2. EXPERIMENT 2

After first experiments of different mixtures, there were already very good stabilization values, so that, there were still so many heavy metals left in our mixtures. As explained in Experiment 1 section, average value of 83% of heavy metals was stabilized. That rate increased to 99,15% in a case. In second experiment, we aimed to see whether the zeolite release the heavey metals that stabilized in Experiment 1. So, the new amounts of heavy metals in our mixture were as in Table 5.3.

Table 5.3 The Heavy Metal Amount Left in the 10% Mixture

Heavy Metal	Amount
Cadmium	0,356 ppm
Cobalt	1,512 ppm
Crom	0,421 ppm
Manganese	0,583 ppm
Nicel	0,889 ppm
Lead	2,170 ppm

In Experiment 2 it is observed that Zeolite does not release what stabilized in Experiment 1 at an average rate of ~97% after a waiting time period of one week. The results can be found in Table 5.4 that shows other mixture results too.

Table 5.4 Stabilization of Heavy Metals with Zeolite (%), Experiment 2

Heavy Metal	10%	15%	20%	30%	40%	50%
Cadmium	98,60	98,85	98,87	98,89	100,00	100,00
Cobalt	99,67	99,60	99,74	99,67	99,47	100,00
Crom	95,49	94,84	94,58	96,24	56,31	100,00
Manganese	94,34	95,94	57,03	68,59	51,70	92,98
Nicel	95,39	97,10	90,63	92,47	62,09	97,30
Lead	96,08	94,39	96,15	95,30	95,72	99,37

5.3. EXPERIMENT 3

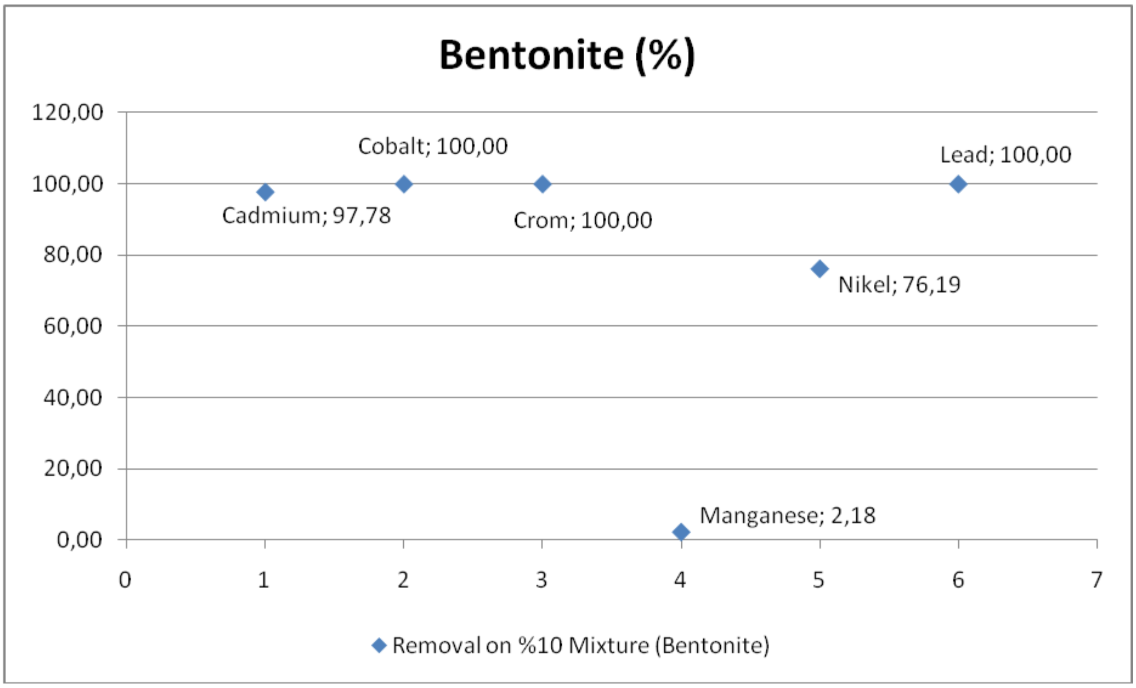

Figure 5.2 Heavy Metal Stabilization in %10 Bentonite & Pure Ash Mixture

The Cd amount in pure ash is 0.36 ppm. But the amount of Cd remains in 10% bentonite + pure ash mixture decreased to 0,008 ppm which means 97.78% stabilization. So, it can be said that bentonite is a good adsorbent at stabilization of Cd in pure ash.

The Co amount in pure ash is 1.525 ppm. But the amount of Co remains in 10% bentonite + pure ash mixture decreased to 0,00 ppm which means 100% stabilization. So, it can be said that bentonite is a good adsorbent at stabilization of Co in pure ash.

The Cr amount in pure ash is 0.445 ppm. But the amount of Cr remains in 10% bentonite + pure ash mixture decreased to 0,00 ppm which means 100% stabilization. So, it can be said that bentonite is a good adsorbent at stabilization of Cr in pure ash.

The Mn amount in pure ash is 1.237 ppm. But the amount of Mn remains in 10% bentonite + pure ash mixture decreased to 0,654 ppm which means 47.13% stabilization. We observed that bentonite have difficulties stabilizing Mn. It is estimated that the reason may be the Mn content in bentonite’s chemical structure.

The Ni amount in pure ash is 1.34 ppm. But the amount of Ni remains in 10% bentonite + pure ash mixture decreased to 0,319 ppm which means 76,19% stabilization. So, it can be said that bentonite is a good adsorbent at stabilization of Ni in pure ash.

The Pb amount in pure ash is 2.33 ppm. But the amount of Pb remains in 10% bentonite + pure ash mixture decreased to 0,00 ppm which means 100% stabilization. So, it can be said that bentonite is a good adsorbent at stabilization of Pb in pure ash.

Although a reasonable stabilization level is observed in 10% Bentonite & Pure ash mixture, more experiments were done with different mixture levels. As in Table 5.5, the stabilization levels in mixtures other than 10% are also resulted in a good way.

Table 5.5 Stabilization of Heavy Metals with Bentonite (%)

Heavy Metal	15%	20%	30%	40%	50%
Cadmium	99,89	100,00	100,00	100,00	100,00
Cobalt	100,00	100,00	100,00	100,00	100,00
Crom	100,00	100,00	99,78	99,10	99,15
Manganese	55,78	32,66	81,89	81,16	59,58
Nicel	87,24	64,25	97,31	95,82	93,28
Lead	98,37	100,00	98,58	98,37	100,00

5.4. EXPERIMENT 4

After first experiments of different mixtures, there were already very good stabilization values, so that, there were still so many heavy metals left in our mixtures. As explained in Experiment 3 section, average value of 79% (95% without manganese) of heavy metals was stabilized. That rate increased to 100% in a case. In second experiment, we aimed to see whether the Bentonite release the heavy metals that stabilized in Experiment 3. So, the new amounts of heavy metals in our mixture were as in Table 5.6.

Table 5.6 The Heavy Metal Amount Left in the 10% Mixture (Bentonite)

Heavy Metal	Amount
Cadmium	0,352 ppm
Cobalt	1,525 ppm
Crom	0,445 ppm
Manganese	0,027 ppm
Nicel	1,021 ppm
Lead	2,330 ppm

In Experiment 3 it is observed that Bentonite does not release what stabilized in Experiment 3 at an average rate of ~97% (without manganese) after a waiting time period of one week. The results can be found in Table 5.7 that shows other mixture results too.

Table 5.7 Stabilization of Heavy Metals with Bentonite (%), Experiment 4

Heavy Metal	10%	15%	30%
Cadmium	100,00	100,00	100,00
Cobalt	100,00	100,00	100,00
Crom	97,30	93,03	99,66
Manganese	-	87,10	74,73
Nicel	91,77	95,04	78,70
Lead	97,00	96,90	98,87

CHAPTER 6

CONCLUSIONS

The producers have to burden the cost of both transportation and removal of wastes. So, economic cost of the high amount of wastes creates difficulties to producers.

More economical alternative methods must be used in removal of hazardous wastes especially in removal of medical wastes.

This study is a result of economic and available solution search of heavy metal removal from medical waste incineration ash. The heavy metals in the ash that results from incineration processes at medical waste incineration plants, intended to be removed by the way of stabilization/solidification.

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