İSTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

ECOTOXICITY EVALUATION OF SLAG FROM SPENT BATTERY RECYCLING: REDUCTION OF LEAD BY STABILIZATION/SOLIDIFICATION

M.Sc. THESIS

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Department of Environmental Engineering

Environmental Sciences & Engineering Programme

JANUARY, 2012

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RECYCLING: REDUCTION OF LEAD BY
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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

HURDA AKÜ GERİ DÖNÜŞÜM PROSESİNDE OLUŞAN CÜRUFUN EKOTOKSİKOLOJİK DEĞERLENDİRMESİ: STABİLİZASYON/SOLİDİFİKASYON YÖNTEMİYLE KURŞUN AZALTIMI

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Vesile Özlem Erkan, a M.Sc. student of İTU Graduate School of Science Engineering and Technology student ID 501101718, successfully defended the thesis entitled "**Ecotoxicity Evaluation Of Slag From Spent Battery Recycling: Reduction Of Lead By Stabilization / Solidification**", which she prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

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FOREWORD

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December 2011   Vesile Özlem Erkan

                                                                            Environmental Engineer

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ABBREVIATIONS

ACF	**:**	Advanced Chemical Fixation
ASTM	**:**	American Society for Testing and Materials
CPR	**:**	Combined Potential Risk
DIN	:	Deutsches Institut für Normung
EEA	**:**	European Environment Agency
EEC	**:**	European Economic Community
EPA	**:**	Environmental Protection Agency
EPT	**:**	Extraction Procedure Toxicity
EU	**:**	European Union
IWT	**:**	International Waste Technology
LDR	**:**	Land Disposal Restrictions
LOEC	**:**	Lowest Observed Effect Concentration
MEP	**:**	Multiple Extraction Procedure
MRF	**:**	Material Recovery Facilities
MSW	**:**	Municipal Solid Waste
NOEC	**:**	No Observed Effect Concentration
NOED	**:**	No Observed Effect Dose
ORV	**:**	Overall Rating Value
RCRA	**:**	Resource Conservation and Recovery Act
S/S	**:**	Stabililization/Solidification
TCLP	**:**	Toxicity Characteristic Leaching Procedure
TAKY	**:**	Tehlikeli Atıkların Kontrolü Yönetmeliği
UN	**:**	United Nations
ZHE	**:**	Zero Head Extraction

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ECOTOXICITY EVALUATION OF SLAG FROM SPENT BATTERY RECYCLING: REDUCTION OF LEAD BY STABILIZATION /SOLIDIFICATION

SUMMARY

The use of lead has evolved over the years, with a significant growth in recyclable uses. One of the main recyclable spent materials is spent automobile battery. The battery-recycling has changed dramatically over the past ten to twenty years as the importance and economy of lead recovery was discovered.

Secodary lead production recently comes out to be a category of industry, other than a recovery facility. With regards to EU directive 91/157/EEC (revised in 2006,2006/66/EC) and Turkish Spent Batteries and Accumulators Control Regulation (Official Journal, 31 August 2004, No: 25569) and, waste accumulators and batteries must be collected separately than other wastes, they must be recycled and recovered or disposed. Battery producers are obliged to ensure or cause to be ensured the collection, recovery, and disposal of spent batteries through participation in a special system. As enforcements are set with these regulations, number of secondary smelting facilities have been increased over the years.

Spent batteries are used as raw materials after they are crushed and separated due to physical/chemical characteristics of content. As describing a secondary lead production industry, their outputs are also needed to be described. Lead containing wastes are highly hazardous and have important impacts on environment. In this research, processes of a secondary lead production facility were investigated and hazardous wastes were examined. Ecotoxicological assessment is performed on lead containing rotary furnace slag. US EPA TCLP test is performed for obtaining eluates for toxicity assay. Stabilization/solidification technique is applied to reduce toxicity of slag. Toxicity tests are applied to both to raw slag samples' and block samples' leachates by using BioTox^{TM}, *Vibrio fischeri* luminescence bacteria.

Metals precipitation of leachates are performed by using NaOH and lime. Recovery of metals ratios from slag leachates is investigated.

HURDA AKÜ GERİ KAZANIMI SONUCU OLUŞAN CÜRUFUN EKOTOKSİKOLOJİK DEĞERLENDİRMESİ: STABİLİZASYON/ SOLİDİFİKASYON YÖNTEMİYLE KURŞUN AZALTIMI

ÖZET

Son yıllarda kurşun tüketimi, özellikle geri dönüştürülebilir kurşun içerikli ürünlerin kullanımı önemli ölçüde artmıştır. Geri dönüştürülebilir kurşun içerikli ürünlerin en büyük bölümünü hurda akümülatörler oluşturmaktadır. Akü geri dönüşüm sektörü özellikle son yirmi yılda, kurşun geri dönüşümünün önemi ve yatırımcıya getirdiği kar nedeniyle çok gelişmiştir.

İkincil kurşun üreticileri, bir geri dönüşüm & geri kazanım tesisi olmaktan ziyade bir endüstri kategorisi olarak karşımıza çıkmaktadır. Avrupa'da (EU Directive 91/157EEC) ve Türkiye'de (Atık Akümülatör ve Pillerin Kontrolü Yönetmeliği, 25569 sayılı Resmi Gazete, 2004) yayımlanan yönetmeliklerin getirdiği ayrı toplama, geri kazanma ve geri dönüştürmek yükümlülükleriyle birlikte, ikincil kurşun üretici firmaların sayısı günden güne artmaktadır.

Türkiye'de günümüzde 12 milyon adet akü üretilmekte ve bu akülerden her yıl 80-120 bin ton atık oluşmaktadır. Hurda olarak nitelendirilen akülerin %90-95 oranlarında geri dönüştürülebildiği söylenebilir. Bununla birlikte, hurda akülerin geri dönüşümünün sağlanabildiği içeriğindeki kurşun ve kurşun bileşenleri en yüksek oranlarda yer almaktadır. Kurşun ve kurşun bileşenleri dışında aküyü oluşturan plastik ve diğer değerli malzemelerden oluşan parçalar da lisanslı firmalar aracılığıyla değerlendirilerek geri dönüşümleri sağlanmaktadır.

Hurda otomobil aküleri bu endüstrilerde üretim hammaddesi olarak kullanılmaktadır. Kırılarak fiziksel ve kimyasal özelliklerine gore ayrılan akü kısımları, her bir kısmın özelliğine gore farklı yöntemlerle geri kazanılır ve geri dönüştürülür. Bu endüstriyi tanımlarken, geri kazanım faaliyetleri sonucu ortaya çıkan atıklar da çok iyi bir şekilde tanımlanmalıdır. Kurşun içerikli atıklar tehlikeli atık olarak değerlendirilmekte ve ciddi boyutta çevresel tehlike oluşturmaktadır.

Tehlikeli atıklar konvansiyonel atıklardan farklı olarak yönetilmesi gereken ve çevre açısından bir tehlike ve zarar kriteri ile ortaya çıkan atıklar olarak bilimsel literatürde görülmektedir. 20-30 yıllık tarihçesi içerisinde çeşitli çevre felaketleri nedeniyle bu atıklara öncelik verilmiş ve yönetimlerinin diğer atıklara göre zahmetli ve zor olduğu anlaşılmıştır. Tehlikeli atıkları diğer atıklardan ayırt edebilme gereği ortaya çıktığında "farklı bir atık" tanımlamak ve bu atık üzerinden tehlike kriteri varsa tehlikeli atık tespiti yapmak mümkün olmuştur. Öte yandan bu tespitler ile oluşturulan yönetmelikler tehlikeli atıkları belirli ölçüde tespit etmesine rağmen tehlikeli olmayan atığı da bu listelerden ayırt etmek gerekmiştir.

Yönetmeliklerin bütün yararlarına rağmen her koşul ve yörede farklı atık türlerine göre statik bir yapı oluşturmaları mümkün değildir. Bu nedenle tehlikeli atık tanım ve

tespitinde tehlike kriteri ile atığın yönetim şekilleri ve diğer bazı faktörler etkin olmaktadır. Tehlikeli atıklar için tehlikeli olma ana kriterleri; parlayıcılık, patlayıcılık, korozivite, reaktivite ve toksisite olarak sıralanmıştır. Bunların yanında kanserojenlik, akümülasyon, tutuşabilirlik, dirençlilik vb. zarar verme potansiyelleri bu kriterler ile birlikte yer almakta ve Birleşik Potansiyel Risk (CPR) olarak bilinmektedir.

Çevre mevzuatı ve yönetmelikleri açısından değerlendirildiğinde çevresel ekosisteme oluşabilecek kurşun sızıntısı farklı yollarla açığa çıkabilecek akü geri dönüşüm endüstrisi atıklarının önemli çevresel etki oluşturmasına neden olan parametreler arasına girmektedir. Ciddi bir atık analizinin yapılarak tesiste oluşan her bir çevre boyutunun değerlendirilmesi gerekmektedir. Daha önce de bahsedildiği gibi atığı tehlikeli yapan kriterlerin her biri için tüm atıklar değerlendirmeyye tabi tutulmalıdır. Tehlikeli atıkların kontrolü yönetmelikleri açısından bakacak olursak Avrupa'da ve Avrupa'dan adapte edildiği üzere Türkiye'de atıklar, içerisinde "ekotoksisite (H 14)" kodunun da yer aldığı 14 tehlikelilik parametresi ile sınıflandırılmaktadır. Ekotoksikolojik olarak atıkların değerlendirilmesine yönelik kimyasallar ile toprağa yönelik tehlikenin belirlenmesi açısından testler yapılmaktadır. Bu testler atıklardan eluat elde edilerek eluatın analiz edilmesi veya atıkların katı formunun analiz edilmesi ile sonuçlandırılmaktadır. Ortaya çıkan konsatrasyon değerine göre oluşturan aralıklardan hangisinin içerisinde sonuçlar kalırsa atığın o sınıfta olduğu –tehlikeli veya tehlikesiz- belirlenmektedir. Genellikle bir atığın tehlikelilik özelliğine karar verilmesi için birleşik risk potansiyelinin her bir kimyasal faktör için değerlendirilmesi ve aynı zamanda doğaya sızma yollarının ortaya koyulması, bu atıkların taşınma, depolama, bertarafı veya yeniden kullanımı sırasında insanların ve diğer canlıların maruziyeti ile sonuçlanabilecek durumların göz önünde bulundurulması ile bir arada değerlendirme yapılması gerekmektedir. Bu nedenle eluat elde edilerek yapılan sızıntı testleri atığın içeriğindeki her bir bileşen için değerlendirme yapmak yerine içeriğin tamamının sızma potansiyelini değerlendirdiği için sucul yaşam ve toprağa etki anlamında tehlikeliliğin belirlenmesinde daha sağlam bir değerlendirme yöntemi olarak karşımıza çıkmaktadır.

Tehlikeli atık olduğu düşünülen atık örnekleri üzerinde tehlike kriterini belirleyecek en önemli deneylerden biri zehirlilik testidir. Bu test çok çeşitli yöntemlerle yapılmasına rağmen atığın formuyla da ilgili olarak ön hazırlık gerektirir. Özellikle katı ve çamur formundaki atıklar için EPT (extraction prosedure toxicity) ya da TCLP (toxicity characteristic leaching prosedure) hazırlığı yapılarak sonuçlar değerlendirilmektedir.

US EPA Toksisite Karakteristiği Sızıntı Prosedürü (TCLP) DIN 38414-4 veya Toksikolojik Ekstraksiyon Prosedürü (EPT) yaygın olarak kullanılan sızıntı testleridir. Yapılan araştırmalar atık kompozisyonundaki bireysel parametrelerin değerlendirilmesiyle karar verilen tehlikelilik özelliğinin her zaman doğru sonuç vermeyebileceği, bireysel değerlendirmenin ötesine geçebilecek, atığın tüm kompozisyonunun çevresel ekosisteme sızıntısının toksisitesini değerlendirecek bir metodun yaygınlaştırılması gerekliliğini işaret etmektedir.

Atıkların ekotoksikolojik olarak değerlendirmesi diğer değerlendirmelere göre daha az sayıda olmakla beraber yalnızca birkaç araştırmanın konusu olarak karşımıza çıkan sızıntı testi ile birlikte ekotoksisite değerlendirmesi yapan çalışma bulunmuştur (Wilke ve diğ, 2008). Aslında, toksisite testleri atıkların toplam kompozisyonunu

değerlendirmek için yapılmalıdır. Bununla birlikte bireysel kirletici parametrelerin limit değerlendirilmesi ve ifade edilmesi, sinerjik veya antagonistik olarak ortaya çıkabilecek özellikleri yansıtmadığı görülmektedir. Yapılan bu araştırmadan sonra bir atığın H 14 tehlike koduna sahip olduğuna karar verilirse bu tehlikeli atığın detoksifikasyonunun sağlanması için uygun arıtma teknikleri araştırılmalı ve uygulanmalıdır. Detoksifikasyon yöntemi olarak çeşitli teknikler çeşitli kimyasallar kullanılarak sağlanabilir. Bu çalışmada stabilizasyon ve solidifikasyon seçeneği değerlendirilmiştir.

İkincil kurşun üretiminden kaynaklanan katı cüruf için ekotoksikolojik değerlendirme sonrasında ortaya çıkan özelliklere göre detoksifikasyon yöntemlerinden en çok kullanılanlardan biri olan stabilizasyon ve solidifikasyon yönteminin uygulanabilirliği araştırılmıştır. Stabilizasyon ve solidifikasyon atık içerisindeki sızma ihtimali olan parametrelerin kimyasal olarak bağlanarak atığın düzenli depolama sahalarına gönderilmeden önce toprağa sızıntı olasılığını ortadan kaldırmak için sıklıkla uygulanan yöntemlerin başında gelmektedir. Genellikle toksik metal içerikli çamur atıklara ve su içeren toksik ağır metallere karşı kullanılan bir yöntemdir.

Bu çalışmada kurşun içerikli cürufun ekotoksikolojik olarak değerlendirmesi yapılmıştır. Değerlendirmesi yapılan atığın ve stabilizasyon/solidifikasyon tekniğiyle farklı oranlarda beton malzeme içerisinde immobilize edilmesiyle ekotoksisite giderilmeye çalışılmıştır. Kullanılan bitüm içinde %25, %50 ve %75 oranlarında kurşun geri dönüşümü prosesine ait döner fırın cürufu eklenmiştir. Toksisite testleri, BioTox^{TM} *Vibrio fischeri* adı verilen bakterilerle gerçekleştirilmiş ve elde edilen EC$_{50}$ değerleri incelenmiştir.

Test yapılan 2,88 ve 4,93 pH değerlerinde cüruf atığından sızan metallerin geri kazanımı ve prosese geri döndürülme verimini hesaplamak amacıyla elde edilen eluatlarda metal çöktürme işlemi uygulanmıştır.

1. INTRODUCTION

The use of lead has evolved over the years, with a significant growth in recyclable uses. Lead has the highest rate of recycling of all metals. Because of its corrosion resistance, lead scrap is available for recycling for decades or even centuries after it is produced.

Today about 80% of lead is used in lead acid batteries, all of which are recoverable and recyclable and recently reported, just under half of the total world lead production of 7.62 million tons comes from recycling of scrap materials (Ellis and Mirza, 2010), [url-1].

Almost 50% of the 1.6 million tons of lead produced in Europe each year has been recycled and is known as secondary lead. The battery-recycling has changed dramatically over the past ten to twenty years as the importance and economy of lead recovery was discovered (IARC, 2011). Changes in secondary lead production market, have resulted with changes from battery-processing technology, changes in battery distribution and sales techniques, changes in lead-smelting technology, changes in the lead alloys used in the batteries and changes in environmental regulation.

With regards to EU directive 91/157/EEC (revised in 2006, 2006/66/EC) and Turkish "Spent Batteries and Accumulators Control Regulation" waste accumulators and batteries must be collected separately than other wastes, they must be recycled and recovered or safely disposed. Battery producers are obliged to ensure or cause to be ensured the collection, recovery, and disposal of spent batteries through participation in a special system (Official Journal, 31 August 2004, No: 25569).

In Turkey, spent lead-acid battery was firstly declared in "Regulation for Control of Hazardous Wastes" published in Turkish Official Journal on 27.08.1995 as "Wastes Requiring Special Processes". In recent version of "Regulation for Control of Hazardous Waste" which was published in Official Journal on 14.03.2005, it is defined under the title of "Special Wastes" with the waste code of "16 06".

Currently in Turkey 12 millions of battery is produced per year 80-120 thousands of tons of spent battery is discarded and spent batteries are recycled with the ratio of 90-95% of total discarded batteries. However big part of the recycling contains production of secondary lead materials and recycling of the plastic materials which are commercially valuable (AKÜDER, 2011), (Recycling Industry, Issue 2, 2007), (Tombul,2005).

From the view of environmental regulations, lead is an important environmental concern as it can be released to environment in many ways from a foundry. A strict waste survey should be done for each environmental aspects of the process. Determination and classification of these wastes are still an area of study which needs specific evaluation for each hazard criterion. From the point of hazard control regulations view in Europe and in Turkey as adapted from Europe, hazardous wastes are classified by 14 criteria including ecotoxicity (H 14). Standardized methods originally developed for chemical and soil testing were adapted for the ecotoxicological characterization of wastes including leachate and solid phase tests. The evaluation of the hazardousness of a waste is commonly done by hazard criteria related with total composition, while potential environmental impact or combined risk potential are evaluated by individual chemicals factors such as release pathways that may result in exposure of man and organisms under conditions of handling, transport, disposal or beneficial use (Sloot and Kosson, 2011). Therefore, leaching assessment instead of total content can provide a much more robust basis for evaluation of potential risks especially for waterborne pathways.

Although The U.S. EPA Toxicity Characteristics Leaching Procedure (TCLP), DIN 38414-4 and EPT are the most commonly used leach tests (Stegemann and Zhou, 2008), various authors claim that, evaluation according to individual parameters analysis in leachates is not sufficient for a determination of ecotoxicity hazard of a waste as those procedures suggest and they have not been yet supported by a measurement of toxicity as a collective parameter (Pandard et al, 2006, Pablos et al, 2009), (Talınlı et al, 2005). Ecotoxicological studies on wastes and waste leachates are relatively scarce, only a few attempts have been made to use leach procedure combined with ecotoxicological tests for the characterization of wastes (Wilke et al., 2008). In fact, toxicity tests should be performed to assess the effect of total composition of wastes, however interpretation and evaluation on the basis of individual parameters and limit concentration values do not seem to reflect synergistic or antagonistic effects.

After those examinations if a waste is determined with H 14 code, appropriate treatment technologies are investigated for detoxification of hazardous wastes.

As slag from secondary lead recycling is a solid and ecotoxic identified hazardous waste, stabilization/ solidification process is one of the most commonly applied techniques for treatment & disposal or reuse as concrete for several uses. Stabilization/ solidification as an immobilization process, it is applied to handle the waste before land disposal, due to the properties of the waste and it is one of the recognized ways to dispose of sludge or water contaminated with toxic heavy metals (Coz et al, 2004, Rha et al., 2000, Angelis et al, 2002, Randall and Chattopadhyay, 2004).

The aim of immobilization is to minimize the rate of contaminant migration into the environment and/or to reduce the pollutant toxicity level, in order to change or improve the characteristics of the waste, thereby making its disposal possible.

1.1 Aim and Scope

Recently, foundries are considered as industries rather than considering recovery facilities only. With this regard, this study focuses on environmental impacts of secondary lead production facilities, especially rotary furnace slag and its toxicity potential.

In this study, leach tests performed on rotary furnace slag, chemical and ecotoxic characterization of leachate are analyzed to conclude toxic the effect of heavy metals.

Toxicity tests were performed for raw slag and after cementation of slag to see reduction in ecotoxicity of this hazardous waste. According to toxicity results possible reuse opportunities and disposal ways were evaluated.

Scope of this study includes:

- Process survey of an existing foundry using spent lead-acid batteries as raw material for production of commercial lead bullions (Pb) and lead monoxide (PbO) with regards to environmental regulations,

- Waste survey conducted according to the mass balance of the processes, especially rotary furnace slag examination and determination of its composition as a hazardous waste,

- TCLP, EPT and DIN 38414-4 leach tests performed in different pH levels and characterization of leachates,

- Toxicity tests performed on leachates by using *Vibrio fischeri*, luminescent bacteria,

- Solidification/ Stabilization application of raw slag and investigation of suitability of land disposal restrictions (LDR), reuse and recovery opportunities by strength tests and detoxification performance,

- Coagulation/ metal precipitation by jar test on raw slag leachates and investigation of feeding the sludge back to the process.

Designation of the waste management system of a battery recycling facility is concluded by the results of the test series above.

2. WASTE MANAGEMENT

Waste management is the collection, transport, processing or disposal, managing and monitoring of waste materials. The management of wastes takes all materials as individually, whether solid, liquid, gaseous or radioactive substances, and tries to reduce the harmful environmental impacts of each waste through different methods.

2.1 Waste Handling and Transport

Waste collection methods vary widely among different countries and regions. Domestic waste collection services are often provided by local government authorities, or by private companies in the industry. Some areas, especially those in less developed countries, do not have a formal waste-collection system.

In Europe and a few other places around the world, a few communities use a proprietary collection system known as Envac, which conveys refuse via underground conduits using a vacuum system. The Envac Automated Waste Collection System is a proprietary waste management system that uses large, underground pneumatic tubes to distribute waste to a centralized processing facility. The system originated in Sweden in the 1960s, and is designed by the Swedish corporation Envac.

In some of the countries, urban centres separate collection is the most common method of disposal, whereby the city collects waste and/or recyclables and/or organics on a scheduled basis. In Turkey domestic wastes are collected material recovery facilities (MRF), then valuable and recyclable materials are separated. A simple waste management circle is given in Figure 2.1.

2.2 Waste Management Concepts

There are numbers of concepts about waste management which vary in their usage between countries or regions. Some of the most general, widely used concepts include:

Waste hierarchy - The waste hierarchy refers to the "3 Rs" reduce, reuse and recycle, which classify waste management strategies according to their desirability in terms of

waste minimization as it can be seen in Figure 2.1. The aim of the waste hierarchy is to extract the maximum practical benefits from products and to generate the minimum amount of waste.

Polluter pays principle: Polluter Pays Principle is a principle where the polluting party pays for the impact caused to the environment. For example, a plant which produces a potentially poisonous output as a by-product of its processes is most of the time responsible for the disposal of that unwanted output safely. With respect to waste management principles, this safe disposal generally refers to the requirement for a waste generator to pay for the treatment of the hazard.

The polluter pays principle was included into United Nations (UN) 1992 Rio Summit.
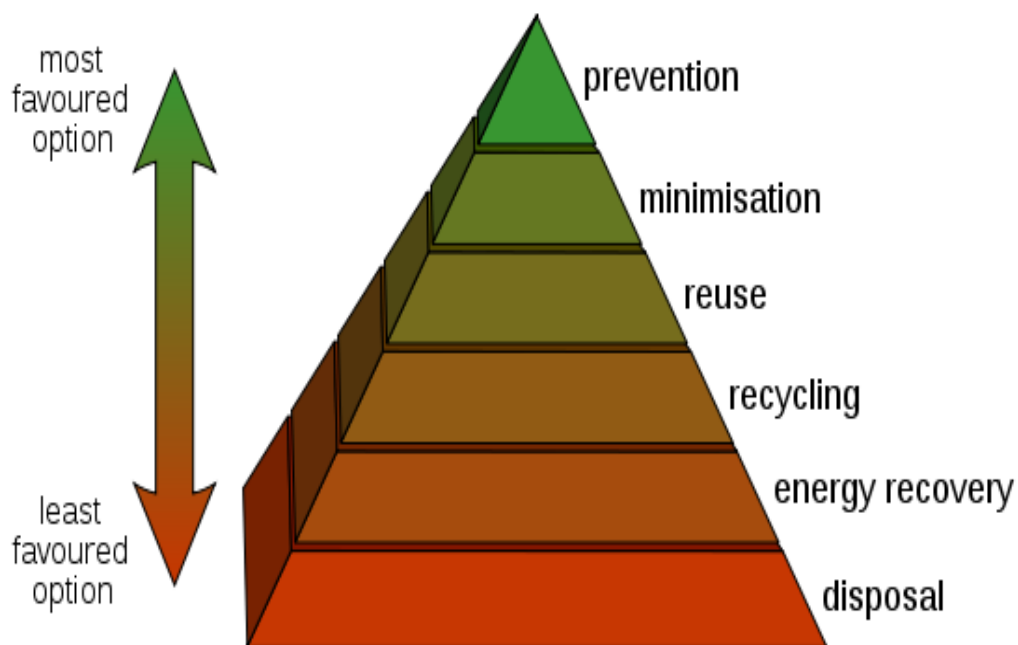
Figure 2.1 : Waste Management Hierarchy.

2.3 Hazardous Wastes

Hazardous wastes, the main drawbacks of industrialized world, are still keeping their importance because of their potential hazard to human health and environment when improperly treated, stored, transported and/or disposed. These types of wastes must be managed and controlled from the point of generation to ultimate disposal (Talınlı et al, 2005).

2.3.1 EPA hazardous waste definition

United States Environmental Protection Agency (USEPA) defines the hazardous waste as a waste which is dangerous or potentially harmful to human health or the environment. Hazardous wastes can be liquids, solids, gases, or sludges. They can be discarded commercial products, like cleaning fluids or pesticides, or the by-products of manufacturing processes (EPA).

EPA regulates household, industrial, and manufacturing solid and hazardous wastes under the Resource Conservation and Recovery Act (RCRA). The Hazardous Waste Program, under RCRA Subtitle C, establishes a system for controlling hazardous waste from the time it is generated until its ultimate disposal which the overall process has become known as the "cradle to grave" system.

In regulatory terms, RCRA divides hazardous wastes into two categories:

1. Listed Wastes, which appear on one of the four hazardous wastes lists established by EPA regulations:

- The F-list (non-specific source wastes)

- The K-list (source-specific wastes

- The P-list and the U-list

F list (Hazardous Wastes From Non Specific Sources): Wastes listed in this type of list are sourced from several industries, public or private corporations and industrial processes. Since sources of these wastes are variety of industries, they are classified in F list as hazardous wastes from non-specific or diffuse sources. K list (Hazardous Wastes from Specific Sources): K list comprises of wastes from several processes of industries as point sources. For this reason, wastes in K list are named as hazardous wastes from specific sources.

P and U list: The commercial chemical products, manufacturing chemical intermediates, or off- specification commercial chemical products are comprised in P and U lists. However, hazardous waste definition of the listed wastes in P and U lists are due to their loss of commercial value, spill or expiry of shelf-life.

Chemicals takes part in P list if the hazard criteria of the chemical is toxicity and it has acute toxicity potential, others take part in U list which are out of expiration date and

useless regardless of hazard criteria. F, K, U and P lists are used for hazard determination of wastes.

2. Characteristic wastes, which exhibit one or more of four characteristics of

- Ignitability

- Corrosivity

- Reactivity

- Toxicity

Although EPA introduces the test protocols for ignitability, corrosivity, reactivity and toxicity, there are still gaps which enable to determine a hazardous waste as conventional waste.

2.3.2 EEA definition

If a waste is identified as hazardous by a specific or general reference to dangerous substances, the waste is hazardous only if the concentrations of those substances are such (i.e. percentage by weight) that the waste presents one or more of the properties listed in Annex III to Council Directive 91/689/EEC. As regards H3 to H8, H10 and H11, limit values for waste to be hazardous are listed in Article 2 of Council Directive 91/689/EEC. For the characteristics H1, H2, H9 and H12 to H14, Article 2 of the directive does not provide specifications at present in EU Waste Catalogue.

In Europe ecotoxicological assessment of wastes is a regulatory requirement. Council Directive 91/689/EEC (EEC, 1991) defines 14 criteria for the characterization of hazardous wastes. The criterion H14 ''ecotoxic'' of Annex III renders ''substances and preparations which present or may present immediate or delayed risks for one or more sectors of the environment'' as hazardous waste (Wilke et al., 2008).

2.3.3 Turkish Regulation on Control of Hazardous Wastes (TAKY)

Wastes having one or more of the hazard properties "explosiveness, flammability, combustibility, productivity of flammable gases, oxidativeness, corrosiveness, causing acute and/or chronic poisoning, leading to infection and forming toxic gas, being ecotoxic and producing liquid extraction" are defined as 'hazardous waste' in Turkish Hazardous Waste Control Regulation. In TAKY, definition of hazardous wastes is mostly similar to EEA. In Annex 7 of the regulation wastes marked with (A) are

defined as hazardous without considering any limit value and wastes marked with (M) are considered as hazardous according to limit values given in Annex 6. Wastes listed according to their natural characteristics or activities they resulted by in Annex 3-A and 3-B, considered as hazardous if they contain the materials listed in Annex 4 and having the properties listed in Annex 5 and hazard properties listed in Annex 6.

2.3.4 Rating systems for determination of hazardous wastes

A rating system for the determination of waste as a hazardous waste was proposed by Talinli and coworkers (Talınlı et al, 2003). Hazard determination of wastes other than conventional wastes overall rating value (ORV) calculates and quantifies the waste as regular, non-regular or hazardous waste in an "hourglass" scale. "ORV" as a cumulative-linear formulation in proposed model consists of components such as ecological effects of the waste (Ee) in terms of four main hazard criteria: ignitability, reactivity, corrosivity and toxicity; combined potential risk (CPR) including carcinogenic effect, toxic, infectious and persistence characteristics; existing lists and their methodology (L) and decision factor (D) to separate regular and non-regular waste.

Although hazardous waste lists and their classification methodologies are nearly the same in most of the countries, there are some gaps and subjectiveness in determining the waste as hazardous waste. A rating system for the determination of waste as a hazardous waste is presented in this study which aims to overcome the problems resulted from the existing methodologies. Overall rating value (ORV) calculates and quantifies the waste as regular, non-regular or hazardous waste in an "hourglass" scale. "ORV" as a cumulative-linear formulation in proposed model consists of components such as ecological effects of the waste (Ee) in terms of four main hazard criteria: ignitability, reactivity, corrosivity and toxicity; combined potential risk (CPR) including carcinogenic effect, toxic, infectious and persistence characteristics; existing lists and their methodology (L) and decision factor (D) to separate regular and non-regular waste. Physical form (f) and quantity (Q) of the waste are considered as factors of these components. Seventeen waste samples from different sources are evaluated to demonstrate the simulation of the proposed model by using "hourglass" scale. The major benefit of the presented rating system is to ease the works of decision makers in managing the wastes (Talınlı et al, 2005).

A rating system was also suggested by Musee and coworkers (Musee et al. (2007) proposed an automated algorithm for waste classification that takes into account physicochemical and toxicity effects of the constituent chemicals to humans and ecosystems, in addition, to the exposure potency and waste quantity. In part I, they described fundamentally contributing properties of wastes to ranking sytem and established facts necessary for the development of fuzzy rule-bases through literature review. They proposed a waste classification ranking index by using the fuzzy set theory for the aggregation of variables and computation.

There are several studies on designation of hazardous waste rating system and classification index, but those have not been accepted and applied in governmental regulations yet.

2.3.5 Landfill of waste

The objective of the Council Directive 99/31/EC is to prevent or reduce as far as possible negative effects on the environment from the landfilling of waste, by introducing stringent technical requirements for waste and landfills.

The directive is intended to prevent or reduce the adverse effects of the landfill of waste on the environment, in particular on surface water, groundwater, soil, air and human health.

Understanding the environmental fate of metals contributed by batteries in a landfill is a function of the conditions of the batteries when landfilled and the conditions of the landfill itself. The casings of household batteries are most commonly made of paper, plastic or metal. The various conditions that can develop in a landfill affect the rate at which the casings will degrade or decompose. The following conditions can affect the rate of degradation: the nature of the casing, the degree of electrical charge left in the battery, the extent of exposure to landfill leachate and the oxygen content of the landfill. The mobility of the metals in a landfill and the potential for groundwater contamination are also controlled by numerous conditions. These conditions include the design, construction, operation and maintenance of the landfill (e.g. the liner, soil characteristics, leachate collection and detection systems, daily cover, final cover, etc.).The release of metals from a battery into a landfill may not however, in and of itself, be problematic. The principal issue is the potential for those metals to contaminate groundwater, which is considered a function of the landfill construction,

its soil characteristics and its distance to groundwater preserves (Bernardes et al, 2004).

Landfilling opportunites of hazardous wastes should be determined by leach tests and due to their toxic characteristic, stabilization/ solidification technique can be beneficial as it is one of the most common applications of treatment methodologies.

2.3.6 Solidification and stabilization

The International Waste Technologies (IWT) Advanced Chemical Fixation (ACF) technology is founded on cement and clay chemistry involving the treatment of soils, sludges and sediments to chemically react, bond or complex with organic and inorganic molecules and ions. The aim of this approach is to prevent leaching of the contaminants above acceptable levels, and to chemically bond or alter to innocuous forms as many of the contaminants as possible and to the maximum degree possible.

There are several features of this technology including:

- Unique organic polymer or silicate-colloid based environments for a durable medium that promotes a variety of bonding mechanisms with a wide range of organic and inorganic molecules;

- Use of admixtures to affect both the internal cement hydration reaction sych that a more effective dispersion of treatment chemicals throughout the waste medium and, externally, to promote certain surfactant functions to promote a microscopic homogeneity of mixing.

The process is based on the use of montmorillonite clays. These clays are notable for the way in which they take up and lose water, and for their high cation and anion exchange capabilities. These abilities are attributable to the alternating layers of alumina and silica and the presence of Group IA and IIA elements (usually Li^+, Na^+, K^+, Ca^{2+}, Mg^{2+} and Fe^{3+}). The treatment of clays such as sodium, magnesium fluorolitsilicate or sodium bentonite, with quaternary cationic species and causes the clay to become organophilic. Further, the quaternary compounds act as pillars and increase the interplanar distances of the clay. The clay will depend upon the type of wastes to be treated. These clays can be mixed with cements or other compounds used in solidification/ encapsulation technologies.

There are two main mechanisms occurring during the reaction process: the relatively fast sorption reaction of the organic or inorganic molecules with the silicate-based macromolecule, and the relatively slower formation of the crystalline structure.

During the sorption reaction, the toxic organic molecules are sandwiched between the alternating layers of silica and alumina, bond with the attached quaternary ammonium compound, and can also strong bond onto the edges of the clay structures.

The second phase of the process involves the slower process of going from a solution, to gel, to the irregular crystalline structure of cementitious material. When cement and slag power are added and hydrated, these materials seal the alumina-organic-silicate layers and crystallize. The principal reactions involved are the hydration reactions of tricalcium aluminate and tetracalcium aluminoferrate. The presence of organics affects this reaction but the sorptive nature of the organic- silicate macromolecule addition at the beginning of the treatment usually prevents too much interference from the organic compounds.

The addition of admixtures causes a more uniform microscopic distribution of the organic-silicate macromolecule throughout the medium being treated. These admixtures have surfactant qualities (wetting, dispersing, emulsifying) to achieve the required distribution and are designed to function in impure environments. The nature of the waste will dictate the type and amound of admixture required.

The material used for solidification/stabilization (S/S) not only solidifies the hazardous waste by chemical means but also insolublizes, immobilizes, encapsulates, destroys, sorbs, or otherwise interacts with selected waste components (Malviya and Chaudhary, 2006).

Stabilization/solidification with cementitious or puzzolanic binders (S/S) is an option for reducing leach ability of contaminants from residual, predominantly inorganic, industrial wastes and contaminated soils before disposal or reuse.

A good understanding of the chemical and physical nature of the waste being treated is necessary to make appropriate decisions regarding treatment, whether or not by S/S. Contaminant concentrations in raw waste are easier to measure than in S/S products, and can be used to calculate concentrations in the treated material. Analysis of the bulk composition and solubility of the raw waste is necessary to understand contaminant speciation and mobility in the waste before treatment, and assess the potential for

interferences with hydration of the cement-based binders, such as binder neutralization as well as acceleration/activation or retardation of setting and/or hardening, false setting, altered water demand and matrix disruption. Waste physical characteristics (e.g., moisture content and particle size distribution) will affect processing and handling. The binder composition will also affect the nature of the hydration and any interference reactions. Characterization of the variability of these raw waste and binder characteristics is critical to interpretation of results from testing of treated products and quality control of full-scale processing (Stegemann and Zhou, 2009).

Stabilization/solidification (S/S) is a very effective tool in the treatment of various wastes, hazardous and non-hazardous.

Stabilization refers to techniques that chemically reduce the hazard potential of a waste by converting the contaminants into less soluble, mobile, or toxic forms.

Solidification refers to techniques that encapsulate the waste, forming a solid material, and does not necessarily involve a chemical interaction between the contaminants and the solidifying additives. The product of solidification, often known as the waste form, may be a monolithic block, a clay-like material, a granular particulate, or some other physical form commonly considered "solid.

Solidification can be accomplished by a chemical reaction between the waste and solidifying reagents or by mechanical processes. Contaminant migration is often restricted by decreasing the surface area exposed to leaching and/or by coating the wastes with low-permeability materials. The combined process of solidification/stabilization mixes wastes, soils, and sludges with treatment agents to immobilize, both physically and chemically, the hazardous constituents in those substances. The technologies are not regarded as destructive techniques; rather, they eliminate or impede the mobility of contaminants (US EPA, 1999).

The stabilization/solidification (S/S) technology is commonly used as the final treatment step for treating hazardous wastes before they are land disposed. It involves adding one or more solidifying agents to a waste to convert it into a monolithic solid with structural integrity. Through S/S, the waste is chemically stabilized and physically modified into a low permeability solid matrix. The leachability of the waste is therefore reduced. The resulting product is also easier to handle and transport (Poon and Lio, 1997).

Quantifying the environmental impact of stabilized/solidified materials in real environmental scenarios is crucial for selecting proper disposal and reuse alternatives and for certification of immobilization technologies. The performance of S/S-treated wastes is generally measured in terms of leaching tests (Jing et al., 2004).

2.3.7 Leach tests

Many batch leaching test protocols have been developed to simulate the leaching processes of waste materials in landfill or other disposal scenarios to evaluate potential risks to human and/or groundwater. The results of batch leaching tests should be carefully evaluated before being used for regulatory or design purposes. The basic objectives of leaching tests are as follow:

- Classify a waste as hazardous or non-hazardous for regulatory application

- Evaluate leaching potential of pollutants resulting from a waste under specified environmental conditions

- Simulate waste or site-specific leaching conditions to evaluate leaching potential

- Provide an extract that is representative of the actual leachate produced from a waste in the field

- Measure treatment effectiveness of a waste

- Identify the appropriate waste management scenario or waste disposal environment

- Determine partition and kinetic parameters for the purpose of contaminant transport modeling (Townsend, 2003)

Sloot and Kosson (2011) described a way how a common set of characterization leaching tests can be used to solve some of the major waste classification issues. They took chemical sludge containing nickel as waste sample to illustrate the approach and carried out several standard leaching procedures. They developed a chemical speciation model on the chemical properties and associated risks in relation to its hazards classifications based on the H categories and risk phases can be obtained from the testing protocols being adopted as standardized testing procedures in CEN, ISO

and US EPA. Their model was not sufficient to find environmentally acceptable solutions for evaluation of ecotoxic wastes.

2.3.7.1 Types of leaching tests

Common batch leaching tests include Extraction Procedure Toxicity (EP-Tox; US EPA Method 1310, 2001), Toxicity Characteristic Leaching Procedure (TCLP; US EPA Method 1311, 2001), Synthetic Precipitation Leaching Procedure (SPLP; US EPA Method 1312, 2001), Waste Extraction Test (WET; California Code of Regulations, 1985), American Society for Testing and Materials extraction test (ASTM D 3987-85, 2001), and Multiple Extraction Procedure (MEP; US EPA Method 1320). The batch tests typically involve mixing size-reduced waste with extraction solution and then agitating the mixture. These tests generally are performed for a short period of time (typically for hours or days) and therefore are often called short -term tests. The main differences among these tests are leaching solution, liquid to solid (L/S) ratio, and number and duration of extraction.

A column or lysimeter test has also been used for simulation of leaching from waste. This test involves the placement of waste material in a column or lysimeter and then the addition of leaching solution to the material to produce leachate. Unlike the batch leaching tests, the leaching solution is under continuous flux. Therefore, this test is often called a dynamic test and may be more representative of field conditions. However, controlling experimental conditions for this test is not easy.

Some operational problems, such as channeling and clogging of the column, may result in a non-reproducible problem. No standardized column test is currently available for experimental uses. Table 2.1 summarizes the main differences between batch leaching and column leaching tests.

Making comparison of the two types of leach tests are between batch and column test while benchmarking two options. Testing period is important in most cases of tests and batch test enables researcher to get results earlier than column tests. Batch tests are easily operated while column test is difficulty operated due to species of wastes. Depending on the test column test need very specific scenario and it has higher cost than designating batch test. Also, batch test enables researcher to control pH with appropriate chemicals while column test does not allow.

Table 2.1 : Comparisons of batch test with column test

Parameters	Batch Test	Column Test
Testing period	Short term (hours to days)	Long term (days to months)
Operation	Easy to operate	Difficult to operate (Channeling due ton on-uniform packing of waste or clogging of column)
Cost	Relatively low	Relatively high
Application of Results	Depending on type of batch test	More specific scenario
pH control	Easy to control pH with appropriate chemical	Material dictates its own chemical environment

Regulatory Leaching Test: Under this title it is discussed and introduced the protocols of regulatory leaching tests that have been widely used in the USA and other countries, especially EU.

US EPA, Toxicity Characteristic Leaching Procedure (TCLP) The TCLP method is one of the most commonly used laboratory leaching tests and was developed to simulate contaminant leaching resulting from waste in a municipal solid waste (MSW) landfill environment.

The Extraction Procedure Toxicity (EP-Tox) test was used to classify wastes as hazardous or non-hazardous prior to development of the TCLP by simulating the leaching process of a waste disposed of in a sanitary landfill. The basic experimental procedure is similar to the TCLP procedure, as described in the following. A 100-g sample of waste (less than 9.5 mm particle size) extracted with deionized water for 24 hours is maintained at a liquid to solid (L/S) ratio of 16:1 (20:1 final dilution), as well as a pH of 5 ± 0.2 using 0.5 N acetic acid. The 20:1 L/S ratio was used based on the assumption that 5 percent of the potentially hazardous waste was co-disposed in an MSW landfill. The acetic acid simulates the organic acids produced from the MSW landfill.

In 1990, the US EPA adopted the TCLP to improve the leaching test procedure and replace the EP-Tox Test. One of the major criticisms of the EP-Tox test was its inaccuracy when organic compounds, especially volatile organic compounds, were

involved. A Zero Head Extraction (ZHE) procedure for volatile organic compounds has been included in the TCLP test.

TCLP Methodology: Developed as a modification of the US EPA's extraction procedure test, the TCLP was intended to simulate the conditions that might occur in a landfill where decomposing garbage is present. The TCLP test involves extracting contaminants from a 100-g size-reduced sample of waste material with an appropriate extraction fluid. A specific L/S ratio (20:1) is employed, and the mixture is rotated for 18 ± 2 hr at 30 rpm. The extraction fluid of TCLP depends on the alkalinity of the waste material. Very alkaline waste materials are leached with a fixed amount of glacial acetic acid without buffering the system (pH 2.88 ± 0.05), while other waste materials are leached with glacial acetic acid buffered at pH 4.93 ± 0.05 with 1-N sodium hydroxide. After rotation, the final pH is measured, and the mixture is filtered using a glass fiber filter. The filtrate is collected in an appropriate container. The filtrate is analyzed for a number of constituents. If these constituents exceed the concentrations describing in 40 CFR 261, the waste is hazardous for the TC (unless otherwise excluded).

The US EPA Synthetic Precipitation Leaching Procedure (SPLP): The SPLP test is performed in the same manner as the TCLP. The extraction fluid is made of two inorganic acids (nitric and sulfuric acid) to simulate acidic rainwater. East of the Mississippi River, the fluid is slightly acidic at a pH 4.22 ± 0.05, which reflects the impact of air pollution due to heavy industrialization and coal utilization. An extraction solution with a pH of 5.0 is used west of the Mississippi River, reflecting less industrialization and smaller population densities. In a similar fashion as the TCLP, a 100-g sample of waste material is placed in a 2-liter extraction vessel and mixed with the extraction fluid. The mixture is rotated for 18 ± 2 hr at 30 rpm. The leachate is then filtered and analyzed for chemical analysis (US EPA, 1996).

California Waste Extraction Test (WET): The WET test is similar to the TCLP in that it uses a buffered organic acid solution as the extraction fluid. This test uses a pH buffered citrate acid solution with sodium hydroxide, a 10:1 L/S ratio, and a 48-hour testing period. The WET extraction solution is prepared with a combination of 0.2 M citric acid solution and 4.0 N NaOH to pH 5.0 ± 0.1. One liter of this solution is added to a 100-g sample and rotated for 48 hours. After rotation, the final pH is measured, and the sample is filtered and analyzed.

The US EPA Multiple Extraction Procedure (MEP): The MEP test involves an initial extraction with acetic acid, which is used to simulate MSW leachate, and at least eight subsequent extractions with an inorganic acid mixture (nitric and sulfuric acids) to simulate acid rain. The MEP test starts with the EP-Tox test run for 24 hours. After the 24-hour rotation period and filtration of the leachate, seven additional extractions are performed on the solid phase of the sample captured on the filter. The extraction fluid is the inorganic mixture with pH 3.0 ± 0.2, which is prepared in the similar manner as the SPLP leaching fluid. During each subsequent extraction, the synthetic rain extraction fluid is added to the waste at an L/S ratio of 20:1, and the mixture is rotated for 24 hours per extraction. After each extraction, the final pH is measured, and the leachate is collected and analyzed. This synthetic rain extraction process is repeated at least eight times. If the concentration of any of the chemical constituents of concern increases over that observed in the seventh and eighth extractions, the extraction should be repeated until the concentration in the extract ceases to increase.

American Society for Testing and Materials (ASTM) test: The ASTM test (ASTM D 3987-85) is a deionized (specifically, Type IV reagent water described by ASTM D 1193) extraction test to simulate a condition in which waste material is a dominant factor in determining the pH of the extract. The test uses a 70-g sample of size-reduced waste material (less than 10 mm) with reagent water using L/S ratio of 20:1 for 18 ± 0.25 hours at 30 rpm. This test has been recommended to determine leachability of inorganic constituents only and is not applicable to organic substances.

Regulatory Batch Tests in European Countries: Many waste leaching tests have been commonly used in various countries for regulatory purposes. The DIN 38414 S4 batch test, which is a standardized German leaching procedure for water, wastewater, sediment, and sludge testing, has been widely used for regulatory purposes. This test uses a 100-g size-reduced sample with unbuffered demineralized water using an L/S ratio of 10:1; the test is run for 24 hours while agitating. In France, the AFNOR X 31-210 batch test for granular solid mineral waste has been employed for regulatory purposes (AFNOR, 1988). The test is similar to the German batch test but uses a smaller particle size (less than 4 mm). In the Netherlands, the availability test (NEN 7341) is the Dutch standard leaching test for assessing maximum leachability of waste for regulatory purposes. The procedure consists of reducing the particle size of waste (less than <125 mm), extracting with leaching solution of pH 7 followed by pH 4 using

nitric acid or sodium hydroxide, and agitating for three hours. The pH conditions are consistently maintained throughout the test. The extract in each step is combined for chemical analysis.

The NEN 7349 test is another Dutch regulatory batch leaching test for granular waste. This test is a serial batch test consisting of five successive extractions of waste material with demineralized water. The test is first run at pH 4 using nitric acid at an L/S ratio of 20:1 for 23 hours, followed by four successive extractions with fresh leaching solution.

Performing all those leach tests are due to make ecotoxicological characterization of hazardous wastes. Main concepts of ecotoxicology, toxicity assays and evaluation is described.

2.3.8 Ecotoxicological evaluation of hazardous wastes

Living organisms are composed of cells, and all cells must accommodate and facilitate a variety of chemical reactions to maintain themselves and perform their functions. Introduction of a foreign chemical into a cell may interfere with one or more of these cellular reactions, leading to impaired cell function or viability. All chemicals are toxic, but the concentration, route of entry, and time of exposure are factors that determine the degree of toxic effect (Blackman, 1996).

Toxicology is the study of how specific chemicals cause injury to living cells and whole organisms. Ecotoxicology is defined as the branch of toxicology that studies the toxic effects of natural or artificial substances on living organisms whether animal or vegetable, terrestrial or aquatic, those constitute the biosphere (Rand & Petrocelli, 1995). Of central importance in both toxicology and ecotoxicology is the relationship between the quantity of chemical to which an organism is exposed, the nature and degree of consequent harmful (toxic) effects (Walker et al., 1996). In the hazardous waste context, toxicity is the ability of a chemical constituent or combination of constituents in a waste to produce injury upon contact with a susceptible site in or on the body of a living organism. Toxicity hazard is the risk that injury will be caused by the manner in which a waste handled (Blackman, 1996).

Chemical constituents of wastes may be acutely or chronically hazardous to plants or animals via a number of routes of administration. Phytotoxic wastes can damage plants when present in the soil, atmosphere, or irrigation water. Phytotoxicity is the result of

a reduction of chlorophyll production capability, overall growth retardation, or some specific chemical interference mechanism.

The risk assessment process for evaluation of a hazardous waste site is a specific example of the more general risk assessment processes used in developing risk-based standards. The risk assessment process usually consists of the following four steps:

- Toxicological evaluation

- Dose-response evaluation

- Exposure assessment

- Risk characterization

Once the toxicological evaluation indicates that a chemical is likely to cause a particular adverse effect, the next step is to determine the potency of the chemical.

The dose-response curve describes the relationship that exists between the degree of exposure to a chemical (dose) and the magnitude of the effect (response) in the exposed organism.

At low dose levels, response may not be evident, but as the amount of chemical exposure increases, the response becomes apparent and increases. Thus, a steep curve indicates a highly toxic chemical; a shallow curve indicates a less toxic substance. The toxicity values derived from this quantitative dose-response relationship can be used to estimate the incidence of adverse effects occurring in humans at different exposure levels. Depending upon the mechanism by which the chemical behaves, the curve may rise with or without a threshold.

Exposure assessment is conducted to estimate the magnitude of actual or potential exposures, the frequency and duration of these exposures, and the pathways which organisms are potentially exposed. The product of the exposure assessment process is an estimation of exposure levels or doses incurred for chemicals of concern.

Risk characterization is the process of estimating the incidence of an adverse effect under the conditions of exposure. It is performed by integrating the information developed during the toxicity assessment and the exposure assessment to yield a complete characterization of risk.
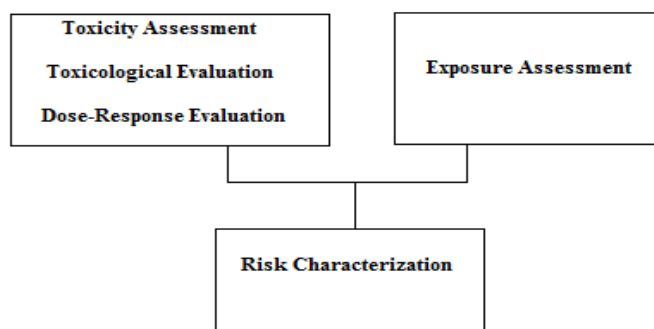
Figure 2.2 : Risk Assessment Process (Blackman, 1996).

A risk assessment process is used to derive a reliable estimate of the amount of chemical exposure which is considered acceptable for humans or other organisms. It is important to recognize that, for many chemicals, current toxicological knowledge is insufficient to answer this question with assurance. It is very basic insufficiency which so frequently causes the standards-setting process to be exceedingly lengthy and/or seemingly endless.

2.3.8.1 Toxicity hazard

In the hazardous waste context, toxicity is the ability of a chemical constituent or combination of constituents in a waste to produce injury upon contact with a susceptible site in or on the body of a living organism. Toxicity hazard is the risk that injury will be caused by the manner in which a waste handled.

Chemical contaminants may be chronically toxic to mammals if they contain materials that (1) are bioaccumulated or concentrated in the food chain or (2) cause irreversible damage that builds gradually to a final, unacceptable level. Heavy metals and halogenated aromatic compounds are classic examples of chronic toxicants.

The US EPA has classified some 35,000 chemicals as either definitely or potentially harmful to human health. A number of them including heavy metals (cadmium, arsenic) and certain organic compounds (carbon tetrachloride, toluene), are carcinogenic. Others, like mercury, are mutagenic and may tend to induce brain and bone damage (mercury, copper, lead), kidney disease (cadmium), neurological damage, and many other problems. Multiple exposures can be additive or synergistic,

but in most cases, the risk resulting from exposure to more than one of these substances at the same time is not known.

2.3.8.2 Aquatic toxicology

Aquatic toxicology focuses primarily on the deviations that are considered to be adverse in nature and on recovery processes in biota that may occur when exposures diminish.

Aquatic toxicology is a branch of science of ecotoxicology that is multidisciplinary in scope and interdisciplinary in practice. Ecotoxicology is defined as the branch of toxicology that studies the toxic effects of natural or artificial substances on living organisms whether animal or vegetable, terrestrial or aquatic, those constitute the biosphere. It also includes the interaction of these substances with the physical environment in which these organisms live.

It is necessary to understand the chemical (e.g. hydrolysis, oxidation and photolysis), physical (e.g. molecular structure, solubility, volatility, and sorption), and biological (e.g., biotransformation) factors that affect environmental concentrations of chemicals, to determine how potentially toxic agents act in the environment and how the environment acts on these agents and to estimate the potential exposure of aquatic organisms.

The physical and chemical properties of aquatic ecosystems can have a profound effect on the biological activity and impact of chemicals. The vulnerability of the aquatic environment to chemical insult depends on several factors, including;

(1) physical and chemical properties of chemical and its transformation products;

(2) concentrations and total loading of the chemical entering the ecosystem;

(3) duration and type of inputs (acute or chronic, intermittent spill or continuous discharge)

(4) properties of the ecosystem that enable it to resist changes that could result from the presence of chemical (e.g. pH buffering capacity of sea water or dissolved organic matter concentrations) or return it to its original state after the chemical is removed from the system (e.g. flushing of water from estuaries by tidal action); and

(5) location of the ecosystem in relation to release site of the chemical.

2.8.3.3 Toxicity testing

Toxicity investigation studies are essential to assess potential hazards to humans through the acute, subchronic, and chronic exposure of laboratory organisms. Toxicity tests are used to evaluate the concentrations of the chemical and duration of exposure required to produce the criterion effects.

There are many different ways in which toxicity can be measured. Many toxicity tests provide an estimate of the dose (or the concentration in food, air or waters) which will cause a toxic response at 50% level, e.g. median lethal dose, the dose that will kill 50% of a population. It is also possible to establish the highest concentration or dose that will not cause an effect (Walker et al., 1996).

Several terms used in relation to toxicity testing require definition. First, in lethal toxicity testing, LD50 represents the medium lethal dose, while LC50 represents the medium lethal concentration. In toxicity tests which determine these values, it is also possible to determine the highest doses or concentrations which cause no toxicity "the No Observed Effect Dose (NOED) and No Observed Effect Concentration (NOEC)" respectively. These values can only be determined in situations where a higher dose or concentration has produced an effect in the same toxicity test. If a test is carried out where the end point is an adverse response other than death, then an EC_{50} or ED_{50} is determined.

However NOEC and NOED values make sense or reasonable only in a test that consists higher dose shown to create an effect. Here the concentration or dose making the effect occur 50% of the population is determined. NOEC can be determined only where Lowest Observed Effect Concentration (LOEC) is calculated; on the other hand there would be no indicators of toxic concentration. A typical dose response curve is shown in Figure 2.2.

On the other hand the use of NOEC and NOED data in ecotoxicology and particularly regulatory aspects of ecotoxicology has been severely criticized since 1990s. Despite these criticisms, NOECs and LOECs are still produced as a conclusion parameter and reported regularly in the literature and baseline of experimental decisions. For instance all of the direct toxicity assessment programs set up to determine the toxicity of discharges.
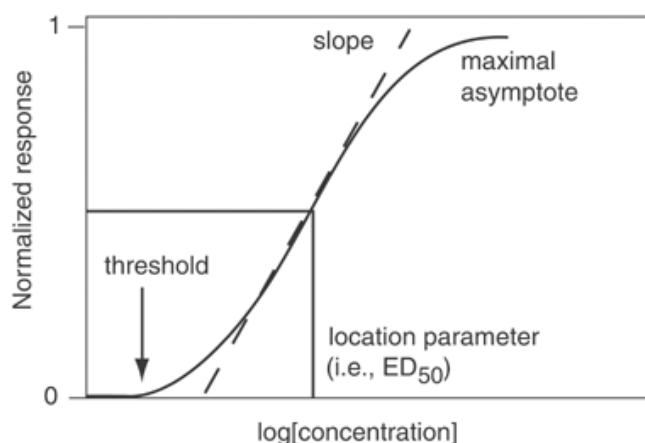
Figure 2.3 : A general dose-response relationship curve

In hazard assessment, a toxicity test can give a plot which relates the frequency of a toxic effect to the dose that is given. This can be compared to a putative "high" environmental concentration to decide whether a hazard exists. A ranking of compounds according to their toxicity is important at this stage. If toxicity is very low, then a compound is not regarded as being hazardous (Walker et al., 1996).

Aquatic toxicity tests are used to detect and evaluate the potential toxicological effects of chemicals on aquatic organisms. Since these effects are not necessarily harmful, a principal function of the tests is to identify chemicals that can have adverse effects on aquatic organisms at relatively low exposure concentrations.

An aquatic toxicity test is frequently called a bioassay and it bioassay refers to specific procedures performed to determine the strength of the chemical from the degree of response elicited in the test organisms, not to estimate the concentration of the chemical that is toxic to those organisms (Rand, 1995).

Bioassay experiments are one approach to evaluate acute toxicity of a composite waste containing numerous constituent chemicals. The bioassay approach provides an accurate and meaningful assessment, because it integrates chemical bioavailability and multiple interactions of all the constituent component effects, whether additive, synergistic or antagonistic in the final measured value (Musee et al., 2007).

Pandard and coworkers (2008) suggested a battery of bioassays for ecotoxicological characterization of hazardous wastes. They developed an experimental test strategy to assess ecotoxicological properties of wastes using a battery of six standardized bioassays. They claimed that, the toxicity-based approach is usually recognized to be

the best method for assessing a potential toxicity for complex mixtures of unknown composition.

In toxicity evaluation process, sometimes risk assessment activities cannot be performed as it takes long time and effort. Decision makers need to make decisions immediately in some cases and there is a rating system to fasten this process. USEPA defines a rating system in toxic substances control act. According to the rating system concentration of a chemical substance which EC_{50} is observed,

- If lower than 1 mg/l highly toxic,

- If between 1-100 mg/l toxic,

- If between 100-1.000 mg/l moderately toxic,

- If between 1.000-10.000 mg/l slightly toxic,

- If higher than 10.000 mg/L not toxic (Talınlı, 2011)

A similar rating is performed by Mantis and coworkers (2005). They classified the toxicity unit (TU) which are:

- TU<1 class 1 no significant toxicity,

- 1<TU<10 class 2 significant toxicity,

- 10<TU<100 class 3 very high acute toxicity,

- TU>100 class 4 very high ecotoxicity

Bioassays by Luminescence Bacteria:

Bioluminescent analytical experiment is one of the most encouraging exact methods for biologically monitoring the aquatic environment because the luminescent system is extremely responsive to even if the media has trace concentrations or amount of pollutants. Bioassays based on luminous bacteria give an complementary prediction of toxicity and constantly exceeding other known bioassays in speed, accuracy, responsivity and its simply design. The enzymes of bacterial luminescent system are also designated in developing extremely responsive analytical methods for practical purposes. Bioassays using luminescence bacteria are widely used for acute toxicity assessment of pollutants. Over the last 20 years, various test procedures using these organisms are applied and validated by several standard organizations. Luminescence bacteria posses some attributes let them suitable for toxicity testing. Their small cells

provide higher surface/volume ratio thus maximizing exposure potential. The close association of the light production pathway with the bacteria's respiratory system provides a convenient and sensitive biological system for quantating a metabolic inhibition due to the presence of toxic chemicals. Those tests are performed by using commonly a saltwater bacteria *vibrio fischeri*. Inhibitions of light production of the cells are determined by exposing them to different concentrations of pollutant solution or leachate. Luminometers are used to measure the light and inhibition after a certain period of exposure. Light production and inhibition of pollutant is compared with a control solution which does not contain any toxic substance. So a correction factor is obtained from the control solution.

The BiotoxTM Software performs automatically all the calculations needed for determining the EC50 value.

$$KF = \frac{IC_t}{IC_0} \qquad (2.1)$$

$$INH\% = 100 - \frac{IT_t}{KF \times IT_0} \times 100 \qquad (2.2.)$$

KF = Correction factor

IC_t = Luminescence intensity of control after contact time

IC_0 = Initial luminescence intensity of cuvette, containing bacterial suspention just before addition of control sample

IT_t = Luminescence intensity of test sample after contact time

IT_0 = Initial luminescence intensity of test sample

In toxicity evaluation a clear term TU, toxicity unit is used which is calculated as "TU=100/EC50".

Determination of toxicity of hazardous wastes needs a special test procedure. Leaching behaviours of hazardous wastes are determined regarding the TCLP, Method 1311, in SW-846 with Zero Headspace Extractor (ZHE) or EPT, DIN 38414-4 and etc. Eluate obtained in different pH values and used for toxicity characterization which is assessment of landfilling or reusing opportunity investigation of a waste, namely a solid to liquid extraction method.

3. SECONDARY LEAD PRODUCTION

Lead reserve all over the world totally has assumed to be 100 million tons and in Turkey 0,8 million tons. Highest reserve values are known to be in Australia, USA, Kazakhstan, Canada and in China. At present time, just under half of the total world lead production of 6 million tones comes from recycling of scrap materials (JMO, 2011). Almost 50% of the 1.6 million tons of lead produced in Europe each year has been recycled and is known as secondary lead. In Turkey 32000 tons of lead is recovered from scrap batteries yearly (Ministry of Environment and Forestry, 2011). Lead uses of materials in the world are listed in Table 5.1.

Table 3.1 : Lead Used Materials (DPT, 2001).

Field of Use	Consumption (%)
Battery Production	60,0
Isolation of cables	5,5
Rolling mill and other products	8,0
Ammunition	2,5
Alloys	4,0
Chemical substances and pigments	13,0
Gasoline additive	3
Other	4
Total	100

Most secondary lead comes from batteries where the primary process involves breaking and smelting used batteries especially lead-acid batteries (EPA 1995). Spent lead acid batteries and the associated manufacturing plant scrap represent over 90% of the contained lead available for recycling. Used automobile batteries represent about

85% of the lead acid battery scrap materials. Other lead recycled scrap materials are sheaths from telephone and power cable, lead pipe and sheet, weights (particularly automobile and truck wheel weights), anodes, printing metals, dross's, residues, sludge's, and dusts.

Primary production of 1 tone of lead requires 345 kWh energy, but for 1 tone lead to recover from spent batteries, only 115 kWh of energy consumed (Ministry of Environment and Forestry, 2011).

3.1 Information About Batteries

A battery is an electrochemical device that has the ability to convert chemical energy to electrical energy. Battery systems are classified according to the materials used as electrodes and basic or acidic electrolyte, materials determine the specific characteristics of the systems. In this study, lead-acid batteries are investigated.

The potentially hazardous components of batteries include lead, copper, zinc, cadmium, manganese, nickel and lithium.

A typical automobile battery is shown in Figure 3.1.

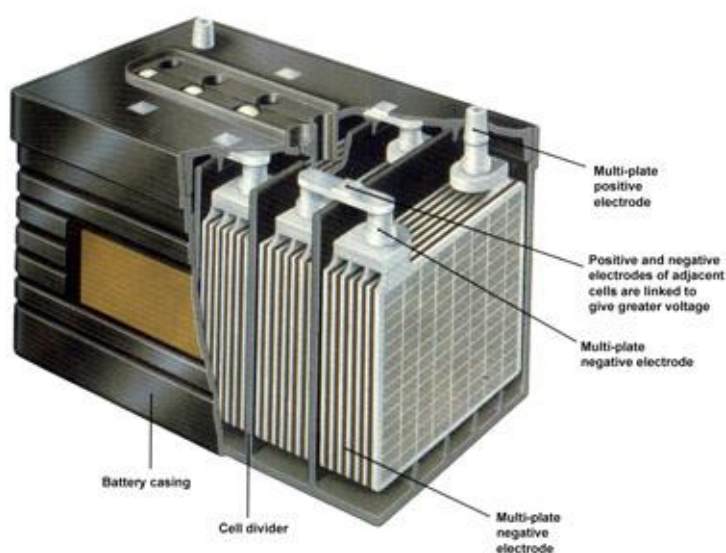**Figure 3.1 :** Lead-acid battery (Prime Products, 2011)

Basically there are two types of batteries (along with subcategories). The two main types are starting (cranking) and deep cycle (marine/golf cart). The starting battery is designed to deliver quick bursts of energy to start engines, and has thinner plates and different material composition. Deep cycle battery seems to have less instant energy.

3.2 Types of Lead-Acid Batteries

Despite the range in battery types and applications, the characteristics particularly important in applications and the maintenance requirements of the battery and the ability to deep charge a battery while obtaining a long lifetime.

Automobile Batteries: The most common type of lead-acid battery is the automotive battery, sometimes called "starting batteries." This type of lead-acid battery has many thin lead plates and is designed to deliver hundreds of amps for a few seconds to start a car. Starting batteries are only designed to cycle about 10% to 15% of their total capacity and to recharge quickly from the alternator after discharging. They are used in motorbikes, automobiles, minibuses, buses, trucks, work machines, marine vehicles, generators and military machines. They have the highest ratio in the battery market. Weights of the automobile batteries are given in Table 3.2.

Table 3.2 : Weights of automobile batteries

Vehicle	Motorbike	Car/ Minibus	Truck	Bus	Tractor
Avg. Weight (kg)	3	15	42	58	28

Stationary batteries: Stationary batteries are often used for emergency power or uninterruptable power supply for communication, transportation, medical services, power stations, control systems, pumping stations, security applications. They are shallow-cycle batteries intended to remain close to fully charged for the majority of their lifetime with only occasional deep discharges.

Traction or motive power batteries: Traction or motive batteries are used to provide electric power for small transport vehicles such as golf carts. Compared to starter batteries, they are designed to have a greater ability to be deep-cycled while still maintaining a long lifetime.

3.3 Battery Components and Properties

The basic battery consists of an anode, a cathode, an electrolyte, separators and the external case. Lead and lead compounds are used as electrodes and dilute sulfuric acid

is used as electrolyte as shown in both figures 1 and 2. Depending upon the capacity of the battery and the field of use, electrode size and number differs.

The modern Lead acid battery is made up of:

A resilient plastic container - usually polyethylene, but increasingly is made from alternative co-polymers or reinforced, but the case material can also be metallic or a synthetic rubber. Positive and negative internal lead plates - The positive electrode (cathode) typically consists of pure lead dioxide supported on a metallic grid, whereas the negative electrode (anode) consists of a grid of metallic lead alloy containing various elemental additives that includes one or more of the following and sometimes others not mentioned, antimony, calcium, arsenic, copper, tin, strontium, aluminum, selenium and more recently bismuth and silver. These alloying elements are used to enhance grid strength, corrosion resistance, reduce over-potential or maintenance, and internal resistance. Porous synthetic plate separators - increasingly made from rib-reinforced polyethylene, but are also available in PVC and fiberglass. The plates are immersed in a liquid electrolyte consisting of 35% sulfuric acid and 65% water. It is the electrolyte that facilitates the chemical reactions that enable the storage and discharge of electrical energy and permit the passage of electrons that provide the current flow. The positive and negative lead terminals used to connect the battery to the car and pass the current from the individual cells via a series of connecting lugs and bridges.

Batteries use a chemical reaction to charge and produce a voltage between output terminals. In Figure 2 structure and chemistry of a lead-acid battery is given.
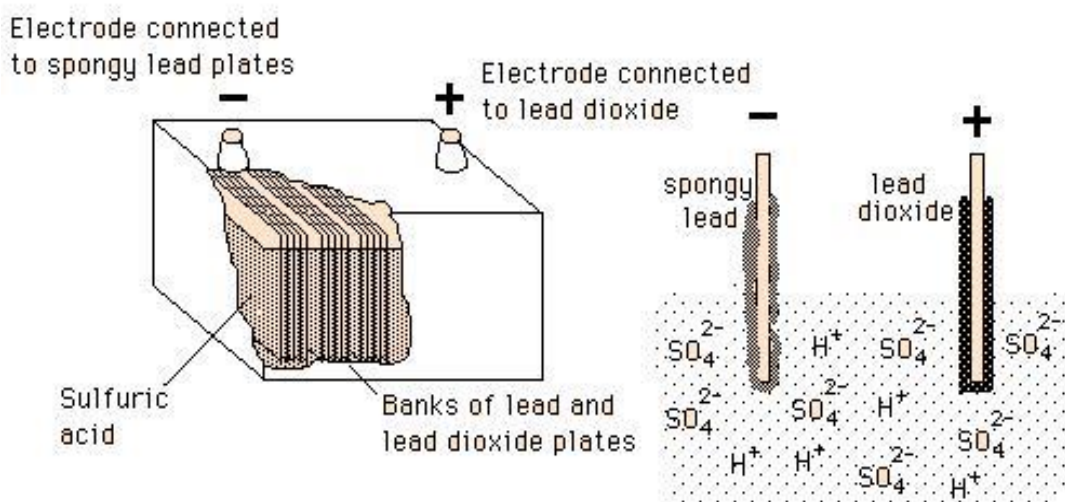
Figure 3.2 : Lead-acid battery and electrodes (Georgia State University, 2011).

In Table 3.3 percentage of composition of a battery by weight is listed. Its composition is comprised of metallic lead by 35 %. It is also contains lead in oxide form as lead oxide with the ratio of 40%. Acidic part which is also as hazardous as lead content is 15%. Other parts have the ratio of 10% in total as plastic coverage or seperators and other residual contents.

Table 3.3 : Composition of a Battery.

Lead- Acid Battery Scrap

Components	% By weight
Metallic Lead	35
Lead Oxide	40
Plastic	7
Acid	15
Residue	3

Battery components containing lead are given in Table 3.4 approximately by percentage of weight. It contains 96-98% of lead in metallic plates and paste is also contained lead in sulphate salt form.

Table 3.4 : Lead containing battery components (Tombul, 2005).

Metallic Plates		44%
Pb	96–98%	
Sb	2–4%	
Ca	<0.5%	
Paste		56%
$PbSO_4$	60%	
PbO (PbO_2)	19%	
Pb	21%	
Total		100%

3.4 Chemistry of a Battery

The chemistry of the production of a voltage by a lead-acid battery is described with the reaction 3.1:

$$Pb^{+2} + SO_4^{-2} \rightarrow PbSO_4 \tag{3.1}$$

Reactions occurring in the lead electrode supplying positive ions and thus remaining negative are given below in equation 3.2, 3.3, 3.4.

$$PbO_2 + 4H^+ + 2e^- \rightarrow Pb^{2+} + 2H_2O \tag{3.2}$$

$$Pb^{2+} + SO_4^{2-} \rightarrow PbSO_4 \tag{3.3}$$

$$PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \rightarrow PbSO_4 + 2H_2O \tag{3.4}$$
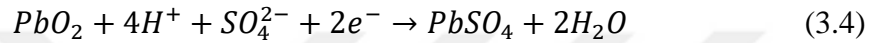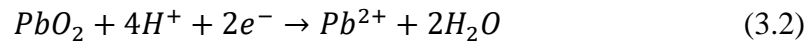
Reactions occurring in the lead dioxide electrode and supplies electron and thus remaining positive are given below in equatins 3.5, 3.6, and 3.7.

$$Pb \rightarrow Pb^{2+} + 2e^- \tag{3.5}$$

$$Pb^{2+} + SO_4^{-2} \rightarrow PbSO_4 \tag{3.6}$$

$$Pb + SO_4^{-2} \rightarrow PbSO_4 + 2e^- \tag{3.7}$$
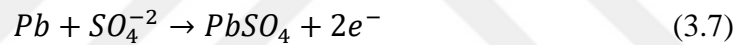
Negative lead electrode and positive lead oxide electrode is shown in Figure 3.3.
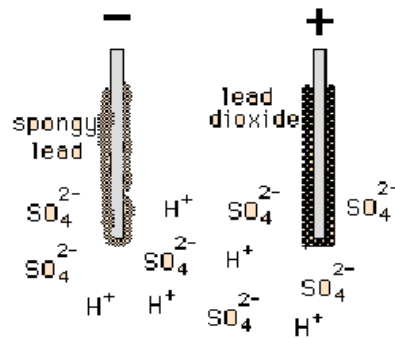
Figure 3.3 : Electrodes of a lead-acid battery (Georgia State University, 2011).

The reaction of lead and lead oxide with the sulfuric acid electrolyte produces a voltage. The supplying of energy to and external resistance discharges the battery. Reaction of a discharge is given in equation 3.8.

$$PbSO_4 + 2H_2O \rightarrow PbO_2 + 2H_2SO_4 + Pb \tag{3.8}$$
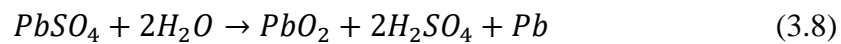
In Figure 3.4 production of a voltage thus discharge of a battery is given.
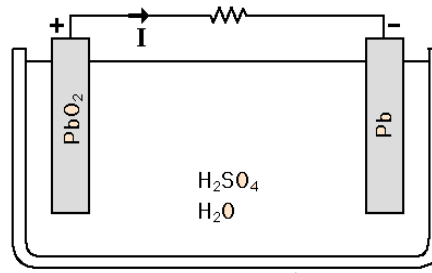
Figure 3.4 : Discharge of the battery (Georgia State University, 2011).

The discharge reaction can be reversed by applying a voltage from a charging source. As given in the Figure 3.5, with energy from the charging battery, the lead sulphate is broken down and with oxygen from ionized water, lead oxide is deposited on the positive electrode and lead is deposited on the negative electrode.

$$PbSO_4 + 2H_2SO_4 + 2PbSO_4 + 2H_2O \qquad (3.9)$$
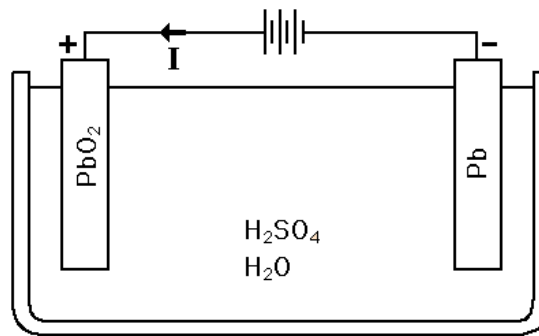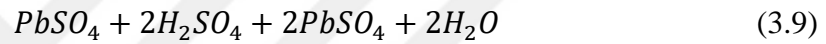
Figure 3.5 : Charge of the battery (Georgia State University, 2011).

Chemical reactions occurring in a battery cell are depending upon the concentration of sulfuric acid as it can also be concluded from the reactions. Total voltage of a cell is calculated by subtracting negative electrode voltage from positive electrode voltage. Voltage changes according to types of electrodes and electrolyte solution.

Theoretically, voltage in a lead-acid battery cell equals:

$V = Vp - Vn = 1.74 - (-0.27) \approx 2$ volts.

Practically, typical value of a cell voltage depending upon the electrolyte density is between 2,05-2,15 volts/cell. Car batteries usually have the capacity of 6 or 12 volts and produced by serially connecting three or six cells.

A lead-acid battery is accepted as discharged when the average cell voltage is less than 1,75 volts. This limit value is determined according to used current. After discharge chemicals on the plates do not convert to other chemical substances totally, chemical energy occurred is converted into electrical energy, partially.

Total amount of energy generated with discharge is called as capacity of a battery. In lead acid batteries, capacity depends on, electrode properties, electrolyte density, conversion ratio of the activated materials covered on electrodes, discharge current value, temperature and minimum voltage taken. In the production process of lead-acid batteries, lead bullions are smelted and alloyed with antimony thus increasing the robustness of plates. Alloys have been given the required shape with casting. On the other hand, lead is used to produce lead oxide, it is mixed with deionized water and sulfuric acid, and lead oxide paste (battery paste) is obtained. This paste is covered to the surfaces of plates and dried. After formation charge of plates, they are put into a case, connected with lead bridges, and divided with separators thus avoiding short-circuiting. After this part of production, electrolytes are added or dry charge batteries are produced.

3.5 Environmental Hazards of Batteries

As major constituent of a lead-acid battery, lead can be taken to human body via drinking water or food chain. When it is intaken to metabolism, body recognizes lead as calcium and accumulates. Accumulation of lead in human body damages to nerve system and causes hearing loss, decrease in hemoglobin concentration, anemia, stomach ache, kidney and brain disease, decrease in fertility, cancer and causes death due to its toxic effects.

On the other hand, electrolyte content of batteries are as hazardous as heavy metals. Release of the sulfuric acid to the environment causes soil, air and water pollution. It necessarily needed to be separately collected, transported and recovered. Sulfuric acid, if contacted to skin or inhaled as vapor damages to body due to its corrosiveness. Repeated and long time inhalation damages to lungs and immune system. Electrolyte in a spent battery has 70 times higher lead concentration than a new one. For this reason, release of electrolytes of spent batteries is a more serious hazard potential for environment (Office of Waste Management, MEF, 2011).

With batteries, the lead can only be obtained by crushing the case. This is commonly done using a battery crushing machine which, in addition to crushing the case, separates out the different components. Thus, the pastes (oxide and sulphate), grids, separators and fragmented cases are all separated from one another. The battery acid is drained, neutralized and disposed of carefully.

The case material is separated by the battery breaker into hard rubber and polypropylene fractions. The hard rubber fraction is either washed or discarded or it can be utilized as a reductant in the smelting process. The polypropylene is subjected to a cleaning and reprocessing operation to make a good quality recycled material. In view of the several colours found in battery case materials, the polypropylene is normally reprocessed to black or other dark shades. Typical applications for the reprocessed plastic are new battery cases, water tanks, videocassette boxes or flowerpots.

3.6 Battery-Recycling

The battery-recycling has changed dramatically over the past ten to twenty years. The changes have resulted from environmental regulation, changes in battery-processing technology, changes in battery distribution and sales techniques, changes in lead-smelting technology, and changes in the lead alloys used in the batteries.

In the 1970s, batteries were distributed primarily through full-service gasoline stations. Smaller amounts were distributed through hardware stores, automobile supply stores, and mass merchandise outlets. The scrap batteries were recovered by the service stations and sold to scrap dealers, who also recovered batteries from wrecked or worn-out automobiles. The scrap dealers then sold the batteries to battery breakers and smelters. The higher lead content of the battery plates made it cost-effective to ship plates longer distances than whole batteries.

In the 1980s, environmental legislation was passed regulating lead acid battery recycling. Rules were promulgated regarding the storage, processing, and transportation of batteries and battery scrap. Batteries and battery components are considered hazardous waste after arrival at a battery breaker or smelter if they are cracked or leaking acid, or if they are disposed of in landfills. Scrap batteries can be stored for only 90 days, after which they must be sent to a recycler or disposed of in a hazardous-waste landfill.

In the late 1970s and early 1980s, several mechanical processes were developed to break the batteries. Technologies were developed to crush the whole batteries, separate the case from the lead-bearing materials, separate the hard rubber (ebonite) and separators from the plastic cases, and, in some cases, separate the paste portion of the battery from the metallic. The acid is neutralized in a separate procedure. A recent innovation desulfurizes the paste, produces lead carbonate, recovers sodium sulfate crystals, and recycles the H_2O. Nearly all battery-crushing processes now recycle the polypropylene battery cases.

3.7 Secondary Smelting

The major smelting processes to recycle lead scrap involve the use of blast furnaces, short rotary furnaces, long rotary kilns, reverberatory furnaces, electric furnaces, and top-blown rotary furnaces.

Blast furnace was used in the secondary industry for many years. However in Europe this has gone out of preference because of the high price of metallurgical coke and the relative difficulty of preventing the escape of dust and fume. The blast furnace was used to provide a low grade antimonial lead, which would be softened - either in a refining kettle or a reverberatory furnace. The high antimony slags would be accumulated for a subsequent blast furnace batch to produce a high amount of antimony bullion for blending into alloys of the desired composition.

In most of the world, rotary furnaces (long, short, and top blown) have replaced blast furnaces as the major smelting vessels for lead recycling. Rotary furnaces are very versatile. They can accept virtually any type of lead-bearing feed material, including battery scrap, dust, dross, scrap lead, and sludge. Rotary furnaces can use any carbon source such as coal, coke, or ebonite as reducing agent, and they can use a variety of fuels, such as oil, coal, or gas. Because they are batch furnaces, rotary furnaces can be operated in stages to produce low-impurity bullion for refining to pure lead, or they can completely reduce the charge to recover all metal values for production of lead-antimony alloys. Rotary furnaces generally use Na_2CO_3 and iron as fluxes, which produce a fluid, low-melting slag.

In stage one; the furnace conditions are held oxidising for antimony but neutral to lead, thus forming antimony oxides which are insoluble in molten lead. In the second stage,

conditions reducing to both lead and antimony are used which reduces any metallic oxides to the metal and liberates carbon monoxide and carbon dioxide (USEPA, 1995).

Stage One:

Battery plates are charged using little or no reducing agent and crude soft lead is tapped off after a few hours with the antimonial slag and lead oxide and sulphate being retained in the furnace. Further plates are charged and more soft lead withdrawn until sufficient slag has accumulated for the slag reduction stage.

Stage Two:

Coke or anthracite fines and soda ash are now charged, both lead and antimony oxides and lead sulphate are reduced and the cycle ends with the furnace being emptied of antimonial lead and of slag for discarding. Lead bullions are shown in Figure 3.6.

Figure 3.6 : Lead Bullions.

Hard rubber battery cases can also be used as co-reductants because of their high carbon content and because of the high cost of metallurgical coke. Iron may be added to the charge in moderate amounts to matte any sulphides produced from the reduction of sulphates and to prevent any sulphurous fumes from leaving the furnace.

Small amounts of lead are recycled via lead sweat furnaces. The primary materials recycled in sweat furnaces are lead-coaled power and communications cable, lead sheet and pipe, and other products that contain lead as a coating or as part of a complex part. The process is performed at relatively low temperatures and produces both metal for refining and slag; the slag is recycled to smelters.

3.8 Raw Material Inputs and Pollution Outputs of Secondary Lead Processing

The material inputs and pollution outputs resulting from primary and secondary lead processing are presented in Table 3.5 adapted from EPA Sector Notebook, Profile for the Nonferrous Metal Industry.

Table 3.5 : Lead Process Materials Inputs/Pollution Outputs (USEPA, 1995).

Process	Material Input	Air Emissions	Process wastes	Other wastes
Lead Sintering	Lead ore, iron, silica, limestone flux, coke, soda, ash, pyrite, zinc, caustic, and baghouse dust	Sulfur dioxide, particulate matter containing cadmium and lead		
Lead Smelting	Lead sinter, coke	Sulfur dioxide, particulate matter containing cadmium and lead	Plant wash down wastewater, slag granulation water	Slag containing impurities such as zinc, iron, silica, and lime, surface impoundment solids (K065)
Lead Drossing	Lead bullion, soda ash, sulfur, baghouse dust, coke			Slag containing such impurities as copper, surface impoundment solids (K065)
Lead Refining	Lead drossing bullion			
Lead-acid battery breaking	Lead-acid batteries			Polypropylene case fragments, dilute sulfuric acid
Secondary Lead Smelting	Lead bullion, soda ash, sulfur, baghourse dust, coke	Sulfur dioxide, particulate matter containing cadmium and lead		Slag, emission control dust (K069)

3.9 Chemical Reactions of Secondary Smelting

As previously described, raw materials obtained from lead-acid batteries:

- Pb (Sb) from plates, terminals and bridges

- PbO (PbO_2) lead oxides (paste)

- $PbSO_4$ lead sulphate (paste)

Whilst first component needs only smelting, to recover lead from other compounds, chemical reactions are needed to be carried out in rotary furnaces.

First, PbO (PbO$_2$) reducted to Pb.

$$2PbO + C \rightarrow 2Pb + CO_2 \tag{3.9}$$

$$PbO_2 + C \rightarrow 2Pb + CO_2 \tag{3.10}$$

Second type chemical reaction produces PbS by reducing PbSO$_4$.

$$PbSO_4 + 2C \rightarrow PbS + 2CO_2 \tag{3.11}$$

Finally PbS is converted to the Pb by the reactions in equations 3.12 to 3.14 below.

$$PbS + Fe \rightarrow Pb + FeS \tag{3.12}$$

Or;

$$PbS + 2PbO \rightarrow 3Pb + SO_2 \tag{3.13}$$

$$PbS + PbO_2 \rightarrow 2Pb + SO_2 \tag{3.14}$$

3.10 Control of Spent Batteries

In the USA, control of spent batteries is described under the Subtitle C of Resource Conservation and Recovery Act (RCRA) of EPA. They are classified as spent materials being reclaimed and they exhibit the toxicity characteristic for lead, and the corrosivity characteristic for the sulfuric acid electrolyte in the battery.

In EU, Council Directive 91/157/EEC 1991 of batteries and accumulators containing certain dangerous substances was published in 1991 and revised in 1996 and 2001. In accordance with the directive accumulator and battery manufacturers, importers, sellers are responsible of their products. Directive includes transportation, recycling and landfilling restrictions of batteries.

In Turkey, spent lead-acid battery was firstly declared in "Regulation for Control of Hazardous Wastes" published in Turkish Official Journal on 27.08.1995 as "Wastes Requiring Special Processes". In recent version of "Regulation for Control of Hazardous Waste" which was published in Official Journal on 14.03.2005, it is defined under the title of "Special Wastes". In accordance with the "Waste Management General Principals Regulation" published in 2008, waste codes for batteries are given in Table 3.6.

Table 3.6 : Waste codes for spend batteries.

Waste Codes	Definition
16 06	Batteries and Accumulators
16 06 01	Lead batteries & accumulators
	Lead batteries
	Lead-acid batteries

In accordance with the Turkish regulation, manufacturers have to recover batteries first year of publication of regulation 70%, next year 80 % and the following year 90% of total produced&imported batteries. 70.000 tons/year battery is released to the Turkish market.

3.11 Battery Statistics in Turkey

Information is provided from the Ministry of Environment and Forestry Special Wastes Statistics document.

3.11.1 Total production and import of batteries

In accordance with "Regulation for Control of Spent Batteries" producers and importers reports, amount of batteries between 2004 and 2009 years are listed in Table 3.7.

Table 3.7 : Battery Production and Import Yearly Amount (Ministry of Environment and Forestry, 2011).

Type	2004 (kg)	2005 (kg)	2006 (kg)	2007 (kg)	2008 (kg)	2009 (kg)
Lead-acid (imported)	15.168.289	20.945.147	22.107.552	24.562.106	30.923.559	28.179.001
Civil aviation vehicles batteries (imported)	183	176	0	0,00	0	0
Production	57.358.400	65.368.368	42.753.316	49.340.000	53.031.000	53.370.000
Total	**72.526.872**	**86.313.691**	**64.860.868**	**73.902.106**	**83.954.559**	**81.549.001**

3.11.2 Manufacturers and importer firms

Number of manufacturers and importers are shown in the Figure 3.7 on a yearly basis between 2005 and 2009 years.

It has been continuously growing and amount of firms have been increasing over the years. Battery firms and reclying facilities have been lisenced by Ministry of Environment and Forestry.
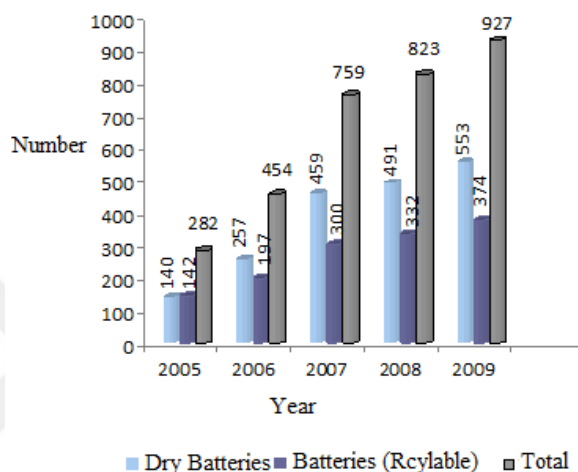

Figure 3.7 : Number of battery firms (Ministry of Environment and Forestry, 2011).

3.11.3 Spent battery collection and recovery

Total amount of collected spent batteries are shown in Figure 3.8 for Turkey between the years of 2005-2009.
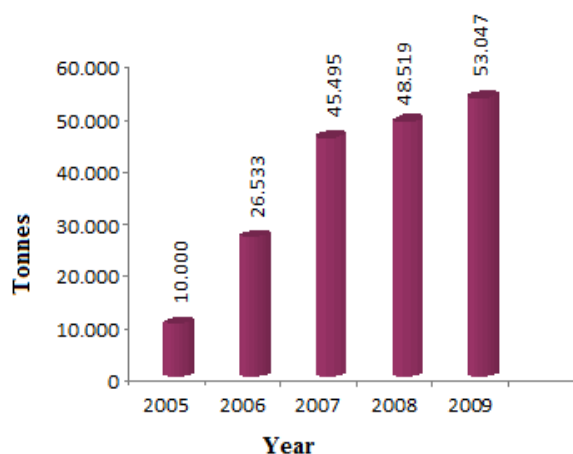
Figure 3.8 : Total amount of collected spent batteries (Ministry of Environment and Forestry, 2011).

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3.11.4 Spent battery recovery facilities (foundries)

Total amount of licenced recovery firms in 2009 and their distribution in Turkey are shown in Figure 3.9.

Figure 3.9 : Spent battery recovery facility distribution in Turkey, 2009 (Ministry of Environment and Forestry, 2011).

After the regulation was published in 2005 number of licensed firms increased by time. Change in number of recovery facilities is shown in Figure 3.10.

Figure 3.10 : Number of recovery facilities between 2005-2009 (Ministry of Environment and Forestry, 2011).

3.11.5 Recovered materials from spent batteries

In accordance with the regulation licensed recovery facilities produces lead. Approximately with the efficiency of 60% lead is recovered. Materials obtained by the

recovery of spent batteries are shown in Figure 3.11, recovery outputs are shown in Figure 3.12.

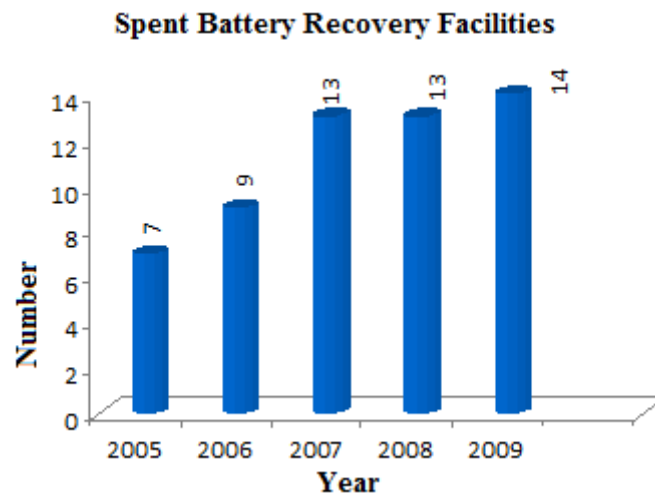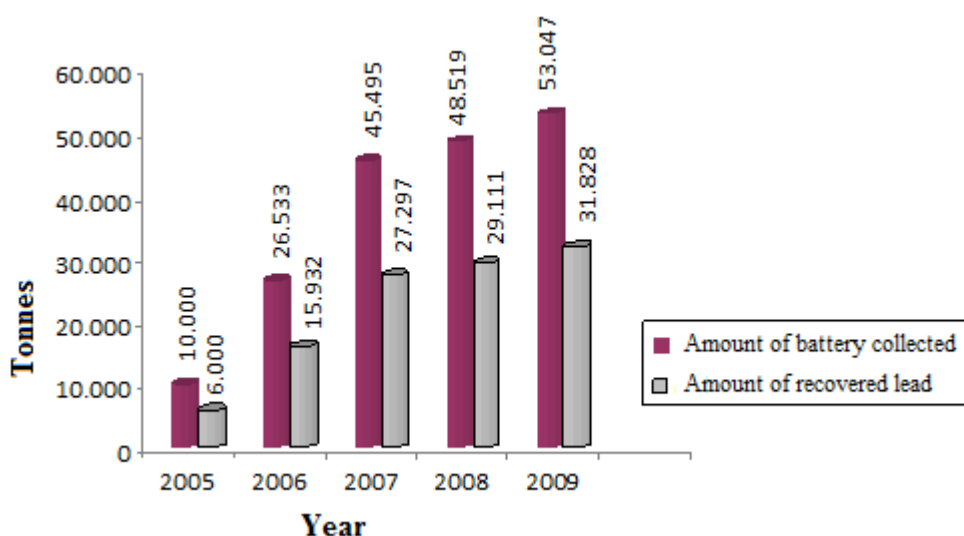**Figure 3.11 :** Yearly collection and recovery amount of spent batteries (Ministry of Environment and Forestry, 2011).

Recovery outputs of spent batteries are given in Figure 3.12.

	2005	2006	2007	2008	2009
lead	6.000	15.932	27.297	29.111	31.828
plastic	1.200	3.186	5.459	5.823	6.366
slag	600	1.593	2.730	2.911	3.183
acid sol.	2.200	5.842	10.009	10.674	11.670
total	10.000	26.553	45.495	48.519	53.047

Figure 3.12 : Outputs of spent battery recover.

3.11.6 Licensed temporary storage facilities

As the regulation consists only 6 collection facility in 2005, it increased to 84 by 2009. Data for the years 2005-2009 is shown in Figure 3.13.
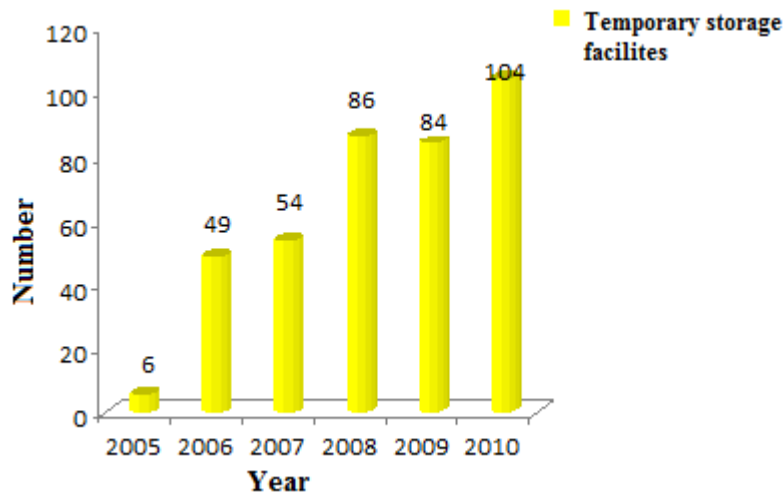
Figure 3.13 : Number of Temporary Storage Facilities 2005-2009.

3.12 Case Study of A Secondary Lead Smelting Facility

A typical lead smelting facility was examined through the secondary production processes of lead oxide, refined lead alloy, refined pure lead for battery industry, construction and for hunting shots.

3.12.1 Capacity of the plant

Smelting capacity: 110 tons/ day, 28050 tons/year

Refinery capacity: 400 tons/ day, 102 000 tons/ year
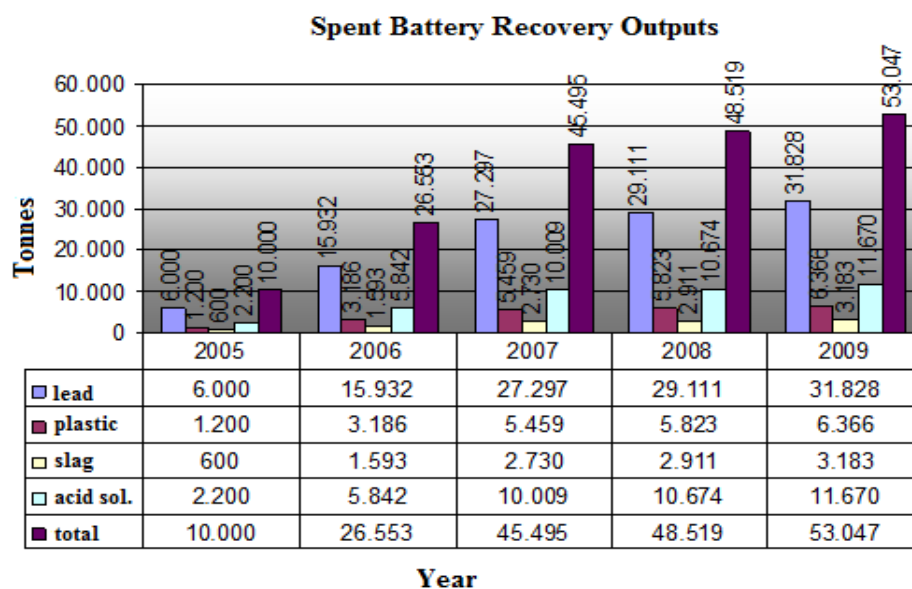
Lead oxide production capacity: 12 tons/day, 3060 tons/ year

Battery crushing-separating process capacity: 120 tons/ day, 36000 tons/year

Process flow of the plant is shown in Figure 3.14.

Products of the plant are listed as follows:

1. Refined specified lead (antiomony alloyed): Used in production of hunting shots in other plant of the same company

2. Refined pure lead: Lead ratio is up to 99,985%, used in battery production plants

3. Refined alloyed (antimony) lead: Battery producers, cartridge production and for users with several purposes.

4. Lead Monoxide (PbO): Battery producers have been directly uses lead monoxide.
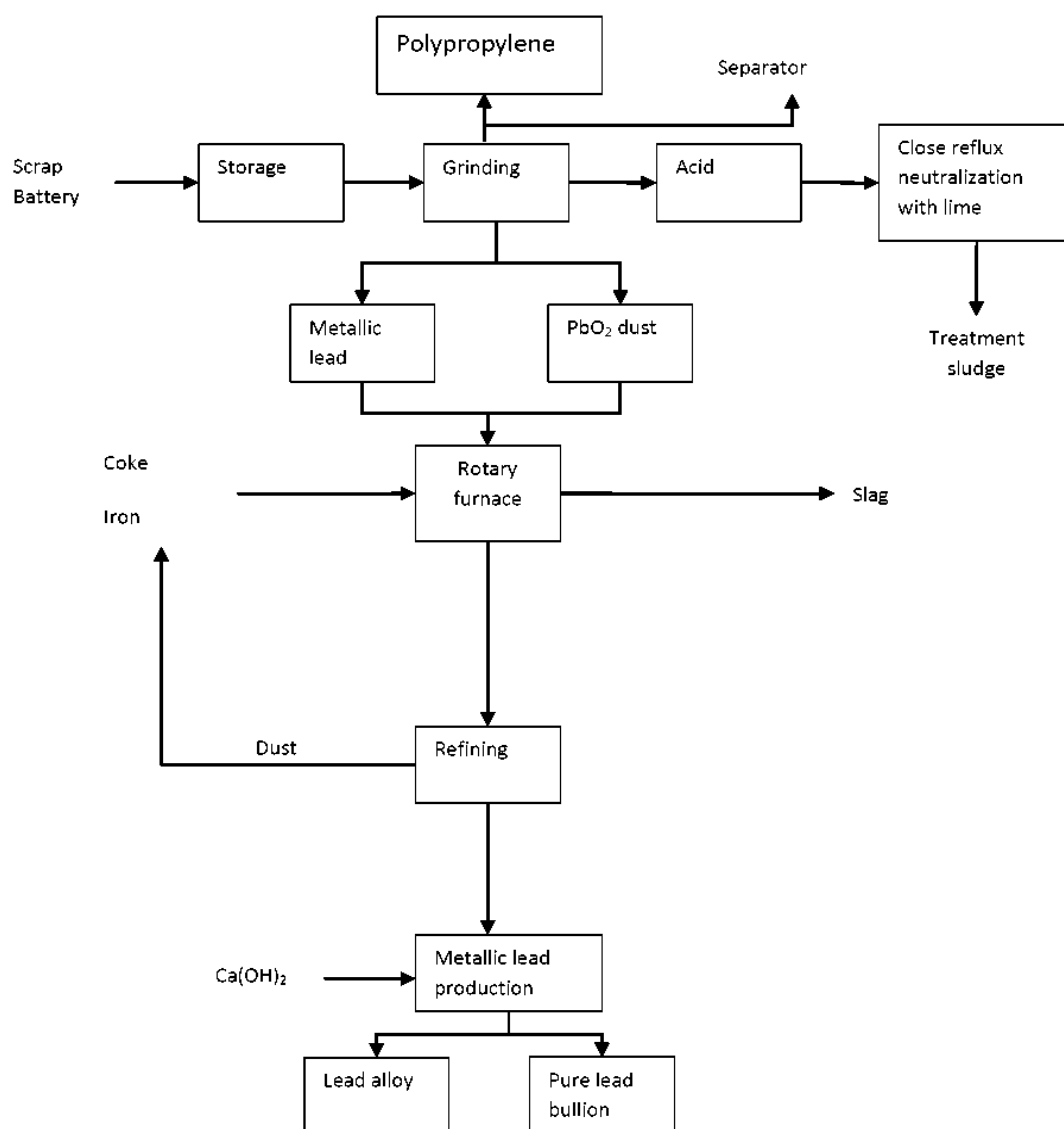
Figure 3.14 : General process flow of the facility.

3.12.2 Processes of the facility

Secondary lead production from spent batteries are provided through the processes explained below. Processes are diversified as crushing, rotary furnace (melting), refining, lead oxide production, storage and neutralization.

Crushing: Crushing and separating, neutralization of acid content and storage is completed in this process.

Rotary Furnace: These processes include rotary furnace raw material storage, furnaces and aspiration, cooling and filter systems.

Refining: Refining pots, aspiration system, bullion machine and hygienic filtration systems are the parts of this process.

Lead Oxide Production: Smelting pots, sizing machinery, elevators, silos, aspiration system, mill, oxide filter system and charging helixes.

Storage and Crushing Unit: Production starts with this process where the spent batteries are taken and stored until they are crushed and the acid content is neutralized.

First stage of the process is grinding and separation of the following different materials:

- Discharged paste, containing lead sulfate (its main compound) and lead oxides;

- Grids and connectors, materials composed mainly of metallic lead;

- Separators, materials composed of plastic, rubber, or cellulose, which prevent contact between the positive and negative plates of the battery;

- Battery casings, materials composed of polypropylene.

Acids of batteries are collected with a drainage system and taken to neutralization-precipitation (N/P) unit. N/P unit comprises of 5 pools and after precipitation of suspended solids, filtrated water is fed back to close reflux system.

Capacity of the crushing unit is 20 tons of battery/ hour averagely. Firstly paste is separated and sent to paste (oxide) silos and dewatered and prepared as a raw material for rotary furnaces.

Separators are transferred to storage by helixes. Plastic parts are sold to licenced recycling & recovery facilities.

Plastic parts could be used as secondary plastic materials production or produced as refuse derived fuel.

Metallic lead parts are also sent to raw material storage for rotary furnace. All materials are separated by using the difference of densities. Storage and crushing units are shown in Figure 3.15 and 3.16.

Genereally a battery recycling plant such as above starts with a helix type loader tips the battery scrap into dosing conveyor which carries the scrap into (rotary furnace). The material is then first crushed in two stages. The back to back sieve and float sink operators generate a capacity of lead enriched product (battery grids and battery terminals, approximately 90% lead, lead oxide, polymer fraction (battery casings). Thus there is a part which also used in other recycling facilities such as plastics.

Figure 3.15 : Storage unit.

Figure 3.16 : Crushing and separating unit.

Neutralization Unit: Acidic content of the batteries are taken to pools and lime is added for neutralization. During this process, as a water treatment, metals and suspended solids are precipitated by adjusting pH to 7,0- 7,5. Treated water is sent back to pools to feed back to the close reflux system and sludge is disposed after dewatering. Capacity of this unit is 20-25 tonnes / day averagely.

Rotary Furnace: Rotary furnace and smelting unit includes raw materials storage, 2 rotary furnaces heaters, circulation pool, pump station, gas cooling and filtration systems.

The paste, grids, connectors, lead dusts recovered from filtration and refining units, rotary furnace slag are fed to the rotary furnaces, where batches of metallic lead is produced. In addition to the lead-containing materials, other materials, such as solid carbon, iron and sodium carbonate, number 4 type fuel oil, are added to the charge of the furnace for lead reduction and recuperation in 1200 ^{0}C.

Solid carbon (coke) is used to reduce the lead present in raw materials, such as $PbSO_4$, PbO_2, and PbO to metallic lead. Iron is added to matte the sulfides produced from the reduction of sulfates and to retain impurities present in raw materials. Rotary furnace is shown in Figure 3.17.
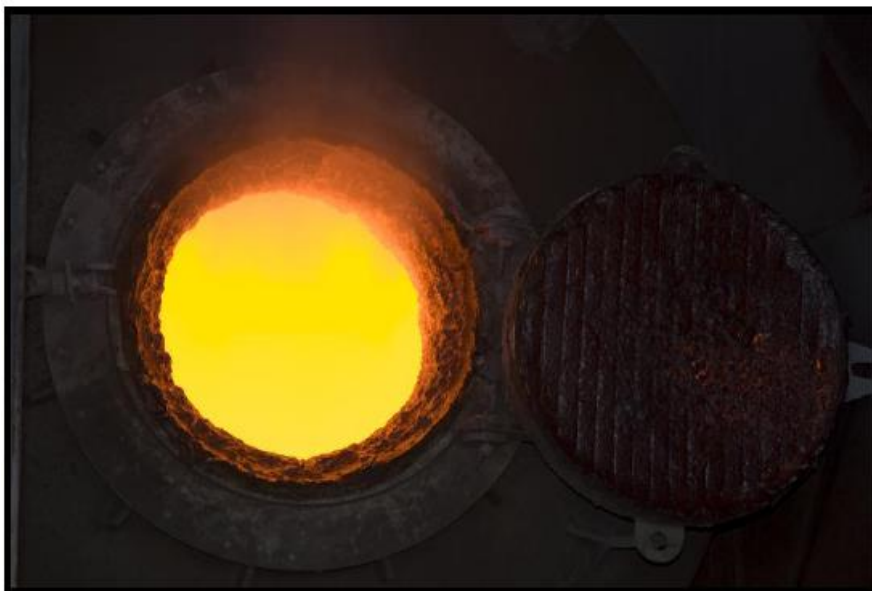

Figure 3.17 : Rotary furnace.

As one of the outputs of rotary furnace is off gas flow resulted by smelting. Off gases from the furnace are first cooled and then passed to a filter unit for fume and dust control. The collected dust is recycled to the furnace feed as recovery of lead dusts. Furnace raw materials storage and filter system is shown in Figure 3.18.

Figure 3.18 : Furnace storage and filters.

As product of the rotary furnace smelted lead mixture is poured into refining pots. After solidification of slag, bottom covers of the pots are opened and high density lead is taken to produce bullions. Bullions are stored according to recipe of the charge of rotary furnace. Typical charge recipe for a batch is given as:

- 4000 kg oxide (paste)

- 4000 kg metallic lead (plates, connectors, bridges)

- 500 kg coke

- 800 kg iron

- 800 kg filter (baghouse) dust

- 800 kg slag matte

- 200 kg caustic soda

Total weight of charge of a batch : 10.300 kg.

Slag is called as nonfluid part separated from the pots. Slag composes of two different parts, one is called as slag matte and slag as the waste of rotary furnace. Slag matte's lead content is recovered after mechanically crushing-separating operation and smelting in rotary furnace in an appropriate amount in the recipe of a charge. Rest part of the slag is disposed via licensed firms.

Refining Pots: In this process, lead refining process is carried out by 100 tonnes capacity of 4 pots, when refined lead is taken from the pots, dust is fed back to rotary furnace. Pots are heated by burning number 4 fuel oil and air mixture. Outputs of rotary furnaces are taken to pots by cranes. Refining operation is performed at temperatures between 300–600ºC. Refining operations are called as pyrometallurgical operations. One of the pots are shown in Figure 3.19.

Figure 3.19 : Refining pot.

Alloying: After refining as pure lead is produced, alloyed lead at different mixing ratios is also produced.

Temperature control is essentially required in this stage. Process is controlled by analyzing the products with a mass based spectroscopy instrument which is shown in Figure 3.20.

Figure 3.20 : Mass spectroscopy laboratory.

After refining is completed fluid lead, pumped into casting machine and bullions are produced in moulds with 25 kg capacity. Lead alloys are shown in Figure 3.21.

Figure 3.21 : Refined lead alloys.

Lead Oxide Unit: This unit is automatically controlled in a different place from the refining pots. 99,99% lead is used as raw material of this process. Lead is charged to melting pots and then sent to alley machine. Alley machine works as rotary and has an individual water cooling system. Alleys are converted into lead oxides by crashing each other, increasing temperature is controlled by a cooling system. Standard value of the product of this process is 70% PbO and 30% Pb relatively. PbO is sucked by aspiration system and collected in filters then sent to storage units by elevators and helixes.

3.12.3 Products

Three main products of the facility are listed as:

- 99.985 % pure lead (25 kg)

- Refined lead alloy (25 kg)

- Lead oxide (50 kg package)

3.12.4 Process based waste definitions

Wastes according to processes above are listed and defined as follows:

Rotary Furnace Slag: Slag is formed as glassy solid in rotary furnace after smelting of the paste, grids and connectors with addition of coke, iron and fuel in 1200 ^{0}C . Pb and Fe is found in this slag and daily generation is 6 tones.

Acid Neutralization Sludge: After crushing of the scrap batteries, acidic part of the bulk is coagulated by lime. This wastewater has a pH value of about "2" and high content of dissolved heavy metals. Sludge is generated by precipitation of metals. Sludge is precipitated as 20% of the treated water by volume. For 1 m^3 of water 1000-1500 kg of sludge occurs. Sludge is taken 5000 kg/ day. Dewatered sludge is 500 kg/ month averagely.

Separators and plastics: After crushing, as major components of a battery of electrolyte and dividing parts which is made of PP (polypropylene) or PE (polyethylene). Separators are obtained 2000 kg/month, according to physical form classification, this type of wastes are defined as solid wastes. A replacement of seperators and placards of a battery is given in Figure 3.22.
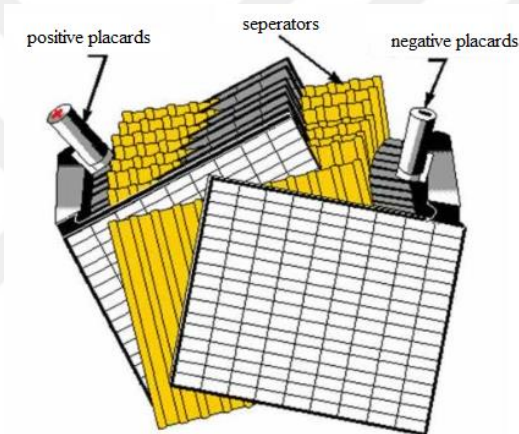
Figure 3.22 : Replacement of a battery

Plastic Recovery Facilities The outer Battery Sells are received and processed in the relative facility into polypropylene chips/granules. The shells are crushed in a polypropylene crusher and the resulting polypropylene parts are either washed and stored, or further processed into polypropylene granules using an extruder machine. Plant designs, fabricate, supply and commission crushers with crushing capacities according to daily production capacity. Those parts should not be dumped directly or as an hazardous waste. Those parts should be disposed to aforementioned recycling facilities .

4. MATERIALS AND METHOD

Leaching of raw slags carried out by performing US EPA TCLP test. The procedure involved agitating 12,5 grams of slag at two different pH levels (pH 4,93 and 2,88) in 250 mL of flask. Elemental analysis were performed for leachates on ContrAA 700^{TM} Atomic Absorption Spectrophotometry. Stabilization/solidification technique is applied and slag is used as construction material in different ratios of block mixtures.

Toxicity tests are applied to both to raw slag samples' and block samples' leachates by using BioTox^{TM}, *Vibrio fischeri* luminescence bacteria.

Metals precipitation of leachates are performed by using NaOH and lime. Recovery of metals ratios from slag leachates is investigated.

4.1 Experimental Approach

Performed experiments are are shown in a flow diagram in Figure 4.1.

The method employed to carry out the leaching process was the toxicity characteristic extraction procedure (TCLP), as found in U.S. Environmental Protection Agency (USEPA, 1995).

The extracted material was vacuum filtered over a 0.45 mm filter. After extraction, all the leachates were kept at 4°C.

Digestion is performed for all samples by using Milestone Ethos One Microwave

The concentrations of heavy metals in the leachates obtained were analyzed by flame atomic absorption spectrophotometry

The inhibition of the luminescence was determined by combining different dilutions of the test sample with luminescent bacteria. The decrease of light intensity was measured after a contact time 5-30 minutes.

Construction materials laboratory was used for this test. Slag samples are crushed into small pieces as small a

Mixtures are shaped in 80 dm^3 blocks and they are shown in Figure 4.11, blocks after 14 days of drying period are shown in Figure 4.1.
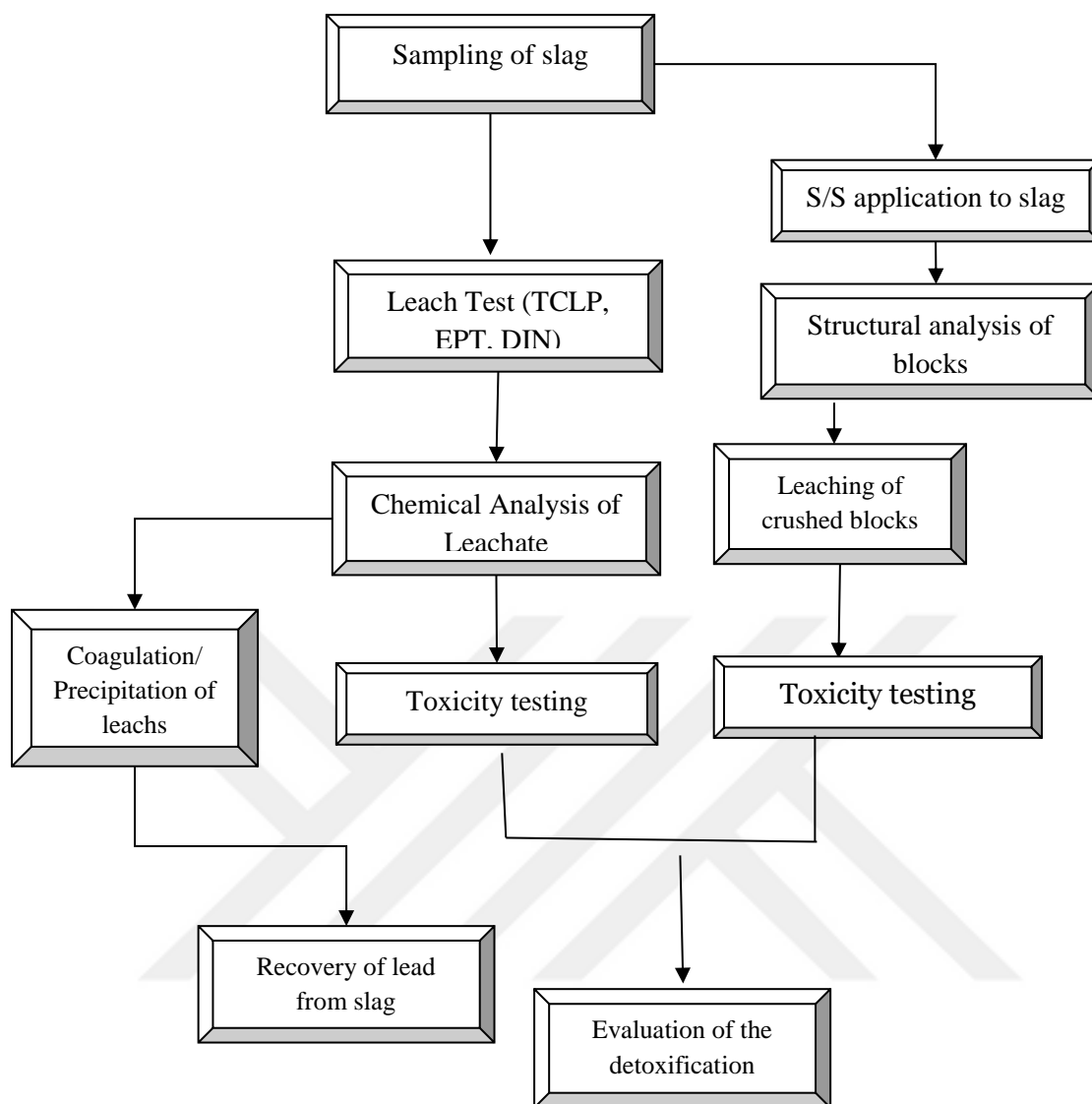
Figure 4.1 : Experimental approach.

4.1.1 Leaching process

The method employed to carry out the leaching process was the toxicity characteristic extraction procedure (TCLP), as found in U.S. Environmental Protection Agency (USEPA, 1995). Once the sample had been homogenized, sub-samples of 12.5 g were taken for each leaching process. Distilled water was added to each solid sample in a volume of 20 times the weight of the slag sample and was continuously stirred for 24 h at room temperature for first samples. Extraction fluids were prepared in two different pH values of 2.88 and 4.93 as recommended in USEPA method:

For pH 4,93, 5.7 mL glacial CH_3CH_2OOH added to 500 mL of reagent water, then 64.3 mL of 1N NaOH added and diluted to a volume of 1 liter.

For pH 2,88, 5.7 mL glacial CH₃CH₂OOH added to 1 L volume of reagent water . 250 mL of extraction fluid is used as 20 times the weight of slag extracted.

4 samples were extracted in pH 4.93 and 5 samples were extracted in 2.88. 5 samples of pH 2,88 and 4 samples of pH 4,93 was shaken during 15 days. Once in three days one sample from each pH value was taken and filtered. Shaker is shown in Figure 4.2.

Figure 4.2. : Constant temperature shaker.

After duration period was complete for each extraction, extract were filtrated through a 45 µm glassfiber filter. Filtrated leachates are shown in Figures 4.3and 4.4.

Figure 4.3 : Lechate filtration.

Filtration was performed either by vacuum system and manually.

Figure 4.4 Raw slag leachate samples

The extracted material was vacuum filtered over a 0.45 mm filter. After extraction, all the leachates were kept at 4°C.

4.1.2 Digestion for metals analysis

To reduce interference by organic matter and to convert metals associated with particulates to a form (usually the free metal) then can be determined by atomic absorption spectrometry or inductively-coupled plasma spectroscopy, use one of the digestion techniques presented below. the least rigorous digestion method was used required to provide acceptable and consistent recovery compatible with the analytical method and the metal being analyzed.

4.1.2.1 Digestion procedure

EPA 3005 A Methodology refers to analyze total dissolved metals. Sample is filtered through 0,45 micrometers filter at the time of collection and the liquid phase is then acidifed at the time of collection with nitric acid.

Samples for dissolved metals do not need to be digested as longas the acid concentrations have been adjusted to the same concentration as in the standards.

Digestion is performed for all samples by using Milestone Ethos One Microwave which can be seen in Figure 4.6. In accordance with the standard methods 7 mL of nitric acid added to 5 mL of sample for digestion as nitrate is an acceptable matrix for both flame and electro thermal absorption. 1 mL perchloric acid was added for complete digestion. Samples after digestion is shown in Figure 4.5.

Figure 4.5 : Microwave digestion instrument (Milestone, Model Ethos One) and digestion vessels after digestion.

4.1.3 Metals Analysis

The concentrations of heavy metals in the leachates obtained were analyzed by flame atomic absorption spectrophotometry, on a ContrAA Model 700 The metals analysed were lead (Pb), iron (Fe), copper (Cu), chrome (Cr), nickel (Ni), cadmium (Cd) and zinc (Zn).

Results are reported as follows:

Metal concentration, mg/L= A x B/C

A: concentration of metal in digested solution, mg/L

B: final volume of digested solution, mL

C: sample size, mL

Metal concentration, mg/kg (wet weight basis)= AxB/ g sample

Metal concentration, mg/kg (dry weight basis)= AxB/ g sample x(100/D)

D: total solids, %

4.1.4 Toxicity assay

The inhibition of the luminescence was determined by combining different dilutions of the test sample with luminescent bacteria. The decrease of light intensity was measured after a contact time 5-30 minutes. The inhibitory effect of dilutions was compared to a toxin free control to give percentage inhibiton (INH%). The value was

plotted against the dilution factor and the resultant curve was used to calculate the EC50 (Effective Concentration causing 50% inhibition of light output) of the samples.

Five different dilutions of samples were prepared as: 2/3, 1/2, 1/3, 1/4 and 1/6. 6 different sample dilutions and a control were prepared with 2% NaCl solution and they were pipetted into cuvettes and duplicate of these cuvettes were stabilized in chiller at 15^0C which is shown in Figure 4.6. 500 µL of bacteria suspension was pipetted to each cuvette and luminescence intensity (I_0) was measured. After initial measurement, 500 µL of sample were added to cuvettes immediately. Sample dilutions containing bacteria were incubated for the chosen contact times (5, 15 and 30 minutes). Luminescence intensity was measured from the first (most diluted) sample and repeated for all samples using the same time interval. Aboatox Model 1253 Luminometer in Figure 4.6 was used to measure luminescence intensity.

Figure 4.6 : Luminometer (Aboatox Model 1253) and Chiller (Aboatox).

4.1.5 Stabilization / solidification (S/S)

Construction materials laboratory was used for this test. Slag samples are crushed into small pieces as small as to pass 3 cm sieve and it is shown in Figure 4.9. Slag, sand, grit and cement as binder were used to prepare blocks. 3 different ratios of slag is studied.

In mixture 1 prepared as a control block and slag is not mixed. In mixture 2, slag ratio was 25 %, and in 3rd and 4th ratios were 50% and 75 %. One of the mixtures and mixing chamber is shown in Figure 4.8. Ratios and weight of materials mixed in blocks are listed in Tables 4.1 and 4.2.

Table 4.1 : Material ratios in block mixtures.

	Mixing Ratios (%)				
	Specific weight (kg/dm³)	BCL	B25L	B50L	B75L
Sand	2,61	25	25	25	25
Crushed sand	2,71	25	25	25	0
Crushed Stone 1	2,72	25	25	0	0
Crushed Stone 2	2,73	25	0	0	0
Slag	3,62	0	25	50	75

Table 4.2 : Weight of materials in $1m^3$ of block mixture.

Component	Block Code			
	BC	B25	B50	B75
Cement (kg)	400	400	400	400
Water (kg)	195,2	195,2	195,2	195,2
Sand (kg)	428	428	428	428
Crushed sand (kg)	445	445	445	0
CS1 (kg)	446	446	0	0
CS2 (kg)	448	0	0	0
Slag (kg)	0	594	1188	1783
Additive (kg)	8	8	8	8
Air (dm³)	30	30	30	30

Block mixtures have been stirred and shaped according to methodology. Aforementioned tables have given the determined ratios of test samples. First block is only made according to standard and does not contain any slag in it. Thus enabling the performance of slag from the strength and suitability.

Figure 4.7 : Slag prepared for S/S.

Figure 4.8 : Mortar.

Mixtures are shaped in 80 dm^3 blocks and they are shown in Figure 4.11, blocks after 14 days of drying period are shown in Figure 4.12. In Figure 4.13 compressive strength test which was performed in construction materials laboratory and in Figure 4.14 crushed blocks for TCLP are shown.

Figure 4.9 : Block preparation.

Figure 4.10 : Blocks with different slag contents.

Slag, sand, grit and cement as binder were used to prepare blocks. 3 different ratios of slag is studied. In mixture 1 prepared as a control block and slag is not mixed. In mixture 2, slag ratio was 25 %, and in 3rd and 4th ratios were 50% and 75 %. One of the mixtures and mixing chamber is shown in Figure 4.10.

Slag, sand, grit and cement as binder were used to prepare blocks. 3 different ratios of slag is studied. In mixture 1 prepared as a control block and slag is not mixed. In mixture 2, slag ratio was 25 %, and in 3rd and 4th ratios were 50% and 75 %. One of the mixtures and mixing chamber is shown in Figure 4.10.

Figure 4.11 : Compressive strength test of blocks.

Figure 4.12 : Block particles crushed for TCLP test.

4.1.6 Coagulation and precipitation

Leachates both with the pH 2,88 and pH 4,93 were mixed in equal volumes. 500 mL of leachates were taken to beakers for the test. Leachate sample is shown in Figure 4.13.

29 mg cationic polyelectrolyte was dissolved in 100 mL of water and added during 15 minutes of slow mixing. Samples mixed rapidly for 1 minute and during rapid mixing NaOH and lime are added for adjusting the pH to an optimum value for precipitation.

1. In first beaker Figure (4.18) NaOH performance was tested.

   3,3 mL of 6 N NaOH added

   1 mL of p.e. was added during slow mixing.,Optimum pH was 9,5.

2. In second beaker lime (Figure 4.19) performance was tested.

   8 g CaO was mixed with 100 mL of water.

   10,5 mL of lime mixture added

   1 mL of p.e. was added during slow mixing:Optimum pH was 9,3.
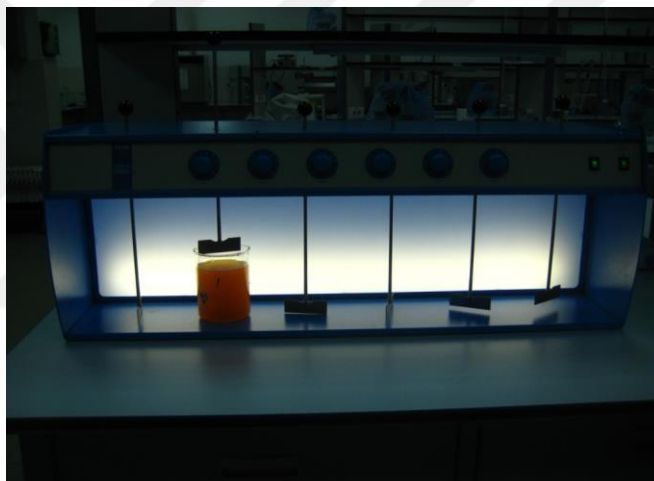

Figure 4.13 : Jar test for leach sample.

Jar test is used to determine the amount of chemicals which should be added to precipitate lead and metallic content of the leachate.

Figure 4.14 : Sludge volume after sedimentation.

5. RESULTS AND DISCUSSION

The results of main experimental sets are discussed as follows:

5.1 Characterization of Samples

Characterization of lead slag from rotary furnace in existing foundry and comparison of other studies are given in Table 5.1. Those results show that lead and iron have been reflected to slag in the same range due to charge of the rotary furnace. Other heavy metal concentrations are not significant except sulphide.

Table 5.1 : Lead slags compositions

	% Contents of raw slag samples (w/w)			
Elements	**Sample of this study**	**Sample of Angelis et al, 2002**	**Sample of Coya et al, 2000**	**Sample of Gomes et al, 2011**
Pb	7,7	16,7	1	1,3- 9,3
Fe	31,4	40,8	40-50	42,4- 57,8
Mn	0,1	0,25	-	-
Zn	0,2	1	0,24	-
Cu	0,5	-	0,44	-
Ni	0,06	0,11	0,03	-
Cd	-	0,02	-	-
Ca	2,1	1,3	1	-
Cl	0,3	0,72	-	-
Cr	0,13	0,07	-	-
K	0,5	0,01	-	-
Mg	0,2	0,3	-	-
Na	1,4	0,4	20-30	3,1-8,6
S	10,6	-	-	2,1-7,1
Sb	0,3	0,27	0,01	-

Metal concentrations in slag leachates are compared to the related regulatory limits and given in Table 5.2 and Figure 5.1. Lead (Pb) contents of LS_1 and LS_2 (this study slag leachate samples) are higher than both US EPA toxicity limits and Turkish regulation hazardous and nonhazardous characterization limits. Other metals except zinc (Zn) are less than aforementioned regulation's limit. Although Turkish regulation is misleading in this subject due to these limits are given as land disposal restrictions these results should be considered as probable synergistic effects in toxicity. Significant difference in solubility was observed only for iron (Fe) concentrations and it is concluded as due to pH differences between LS_1 and LS_2 at pH 4,93 and 2,88 respectively. For the sample LS_3 which is obtained by the extraction procedure toxicity (EPT) and DIN 38414-4 at the pH of 7.0, all of the metals measured was under the AAS detectable limits.

Table 5.2 : Metal concentrations of slag leachates and regulatory limits.

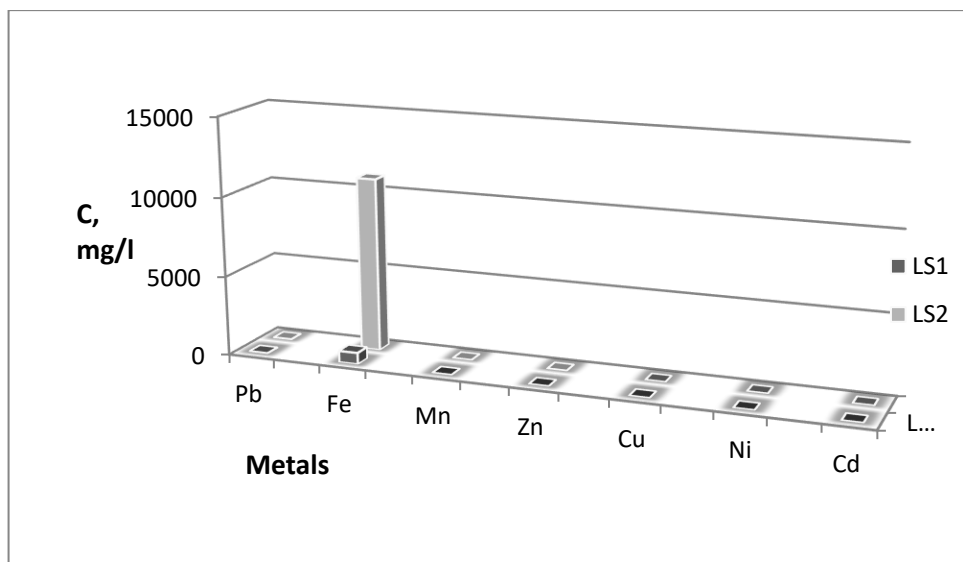| Sample	LS_1 pH 4,93	LS_2 pH 2,88	LS_3 pH 7,0	Angelis et al, 2002	Coya et al 2000	US EPA Min conc. tox	Turkish regulation Annex 11A Nonhazardous	Turkish regulation Annex 11A Hazardous
Pb (mg/L)	31,2	33,9	<1	850	3-75	5	<0,05	<1-5
Fe (mg/L)	722	10920	<0,3	6,6	30-450		-	-
Mn (mg/L)	5,6	12,2	<0,1	4,9	-		-	-
Zn (mg/L)	4,1	14	<0,05	2,5	9-30		<0,4	<5-20
Cu (mg/L)	<0,3	<0,3	<0,3	1,9	0,04-1		<0,2	<5-10
Ni (mg/L)	<0,3	<0,3	<0,3	1,4	1,7-3,4		<0,04	<1-4
Cd (mg/L)	<0,05	<0,05	<0,05	0,4	0,4-1,2	1	<0,004	<0,1-0,5

Figure 5.1 : Metal concentrations levels of the leachate samples.

In Table 5.3 and Figure 5.2 metal concentrations of leachates of crushed blocks with 14 days setting period are given. Lead and iron concentrations were under the detectable limits of AAS and also under the minimum toxicity limits for only control block and 25% slag containing block. Unfortunately, for 50 and 75 % slag containing block leachates metals concentrations exceeds the limits of minimum toxicity and land disposal restrictions (LDR) limits. Stabilization/ solidification fails on detoxification of blocks containing higher than 25% slag ratio. As leachate of raw slag pH 7 does not show any toxicity, slag containing bloks do not show any toxicity in their leachates. Furthermore, this enables us to conclude toxicity is related with the acid use in leach procedures.

Table 5.3 : Metal concentrations of leachates of crushed blocks.

Sample	BCL	B25L	B50L	B75L
Pb (mg/L)	<1	<1	4,1	14,6
Fe (mg/L)	<0,3	<0,3	101,1	127,2
Mn (mg/L)	<0,1	<0,1	<0,1	<0,1
Zn (mg/L)	0,90	1,65	0,74	1,07
Cu (mg/L)	<0,3	<0,3	<0,3	<0,3
Ni (mg/L)	<0,3	<0,3	<0,3	<0,3
Cd (mg/L)	<0,05	<0,05	<0,05	<0,05

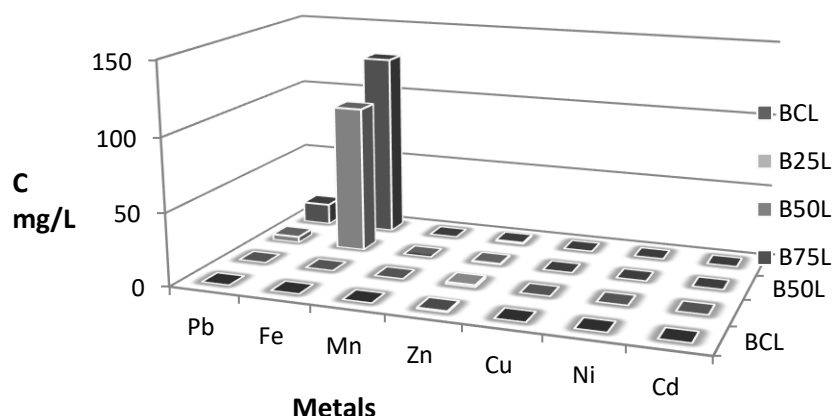*(<): under detectable limits of flame AAS.

Figure 5.2 : Metal concentration levels of crushed block leachates.

5.2 Toxicity Tests

Toxicity test results for samples LS1 and LS2 are given in Table 5.4 and Figures 5.3 and 5.4.

After 5, 15 and 30 minutes of exposure of *Vibrio fischeri,* 50% inhibition values were reported and used for toxicity unit (TU) calculations. EC_{50} values were obtained for very low concentrations of leachates thus making them highly ecotoxic. As higher concentrations of metals are obtained in the LS_2 due to its lower pH value, toxicity unit was calculated approximately 10 times higher than LS1. Toxicity test on eluate which is obtained by EPT at pH 7.0, does not reflect any toxicity thus it has a TU unit of "1" which is not in the ecotoxic range.

Table 5.4 : EC_{50} values and toxicity unit (TU) calculation of slag leachates.

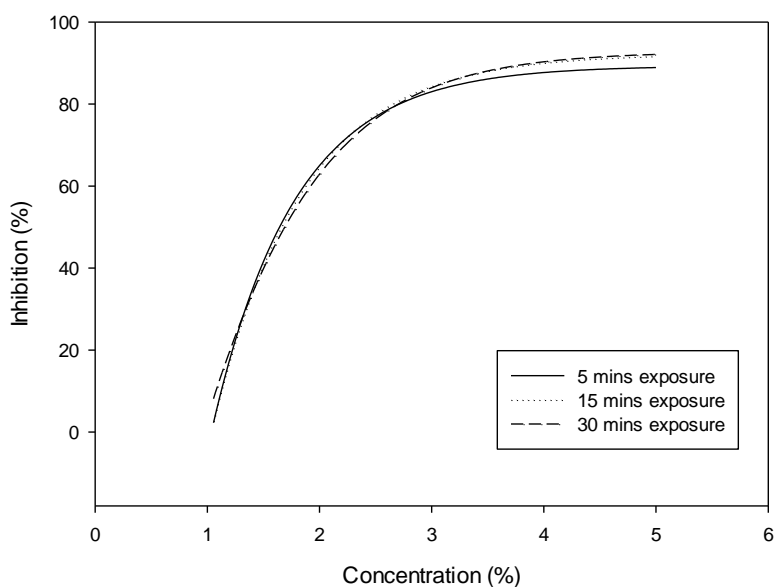| Leachates	LS1 pH 4,93	LS2 pH 2,88	LS3 pH 7,0
EC_{50}: 5mins	1,64%	0,27%	>100
15mins	1,70%	0,23%	>100
30 mins	1,70%	0,20%	>100
TU(100/EC_{50}):			
5 mins			
15 mins	61	370	1
30 mins	59	435	1
	59	500	1

LS1

Figure 5.3 : Relation of raw slag leachate concentration vs inhibition at pH 4,93.
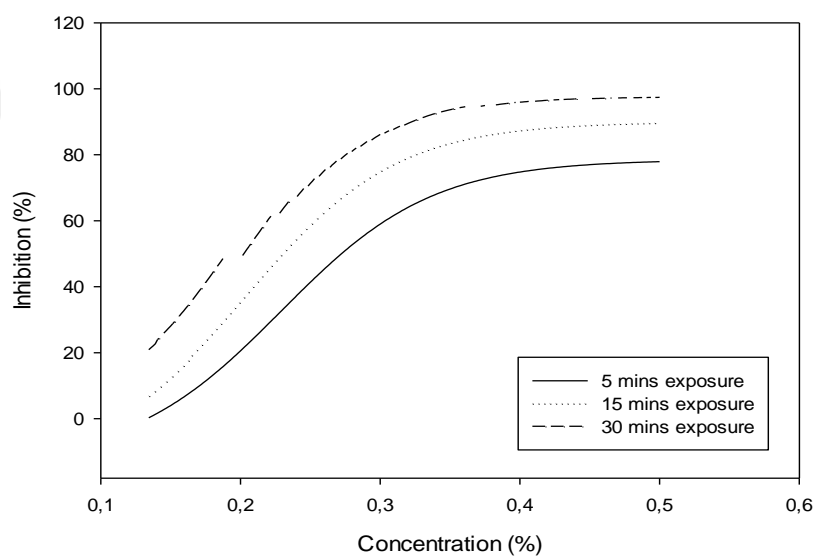
LS2

Figure 5.4 : Relation between raw slag leachate concentration and inhibition at pH 2,88.

In Table 5.5 EC_{50} and TU values of block leachates at 4,93 pH values and in Figures 5.5- 5.8 graphical interpretation of EC_{50} for 5,10,15 minutes of exposure periods of block leachates are given. According to those results, in terms of ecotoxicity, even control block sample which does not contain slag in it, gives "3" unit of toxicity due to probable synergistic effects. Individual parameters analysis of the control block and

25% slag containing block leachates have very low concentrations of metals which do not exceed the minimum toxicity levels and acceptable for the LDR. It also explains that evaluations based on individual concentration of contaminants are not sufficient for determination of toxicity.

Although pH of the block leachates are corrected with a pH control sample, acetic acid may be affecting the toxicity as well as any possible synergistic effect. After 14 and 28 days of mechanical improvement period of blocks, leach tests at pH 7 do not result with any significant toxicity. When TCLP is performed, toxicity seems to be due to effect of pH. Conclusively, solidification/ stabilization technique is applicable under the ratios of 25% of slag as results show after 14 days setting periods of blocks. Blocks containing 50% and 75% slag, allows to leach lead (Pb) and iron (Fe) higher than the limit values thus showing ecotoxicity.

Table 5.5 : EC_{50} values and toxicity unit (TU) calculation of block leachates and Concrete Class of blocks according to compressive strength tests.

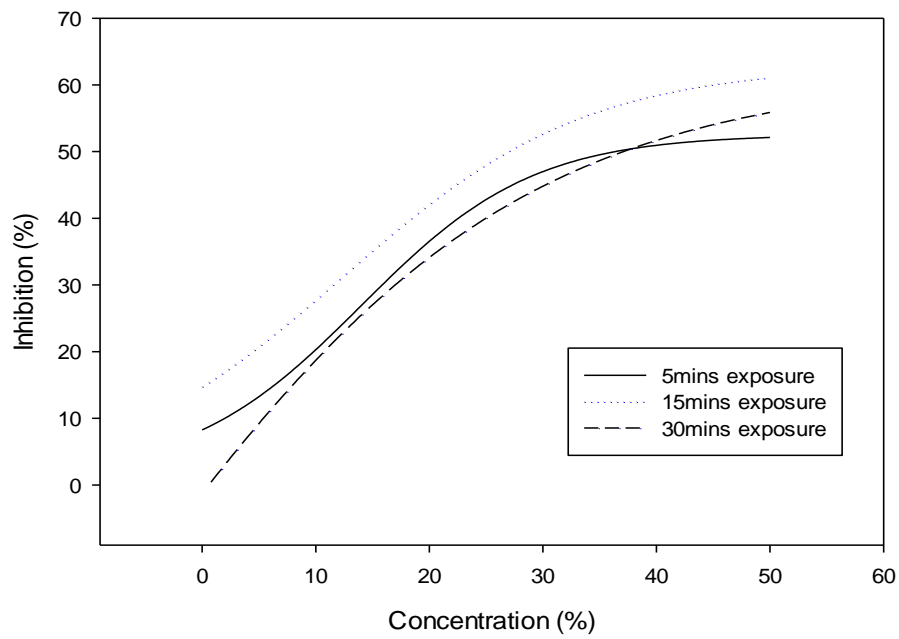| Samples	Leachate EC_{50}	Leachate TU $(100/EC_{50})$	Concrete Class (TS EN 206-1)
BC	5 mins: 36 % 15 mins: 27 % 30 mins: 37 % **Avg:** 33%	3	**C45**
B25	5 mins: 23 % 15 mins: 23 % 30 mins: 29 % **Avg:** 25%	4	**C50**
B50	5 mins: 2,6 % 15 mins: 2,5% 30 mins: 2,7 % **Avg:** 2,6 %	38	**C50**
B75	5 mins: 1,4 % 15 mins: 1,1% 30 mins: 1,1% **Avg:** 1,2%	83	**C40**

BCL 14 days

Figure 5.5 : Relation of control block leachate concentration vs inhibition.
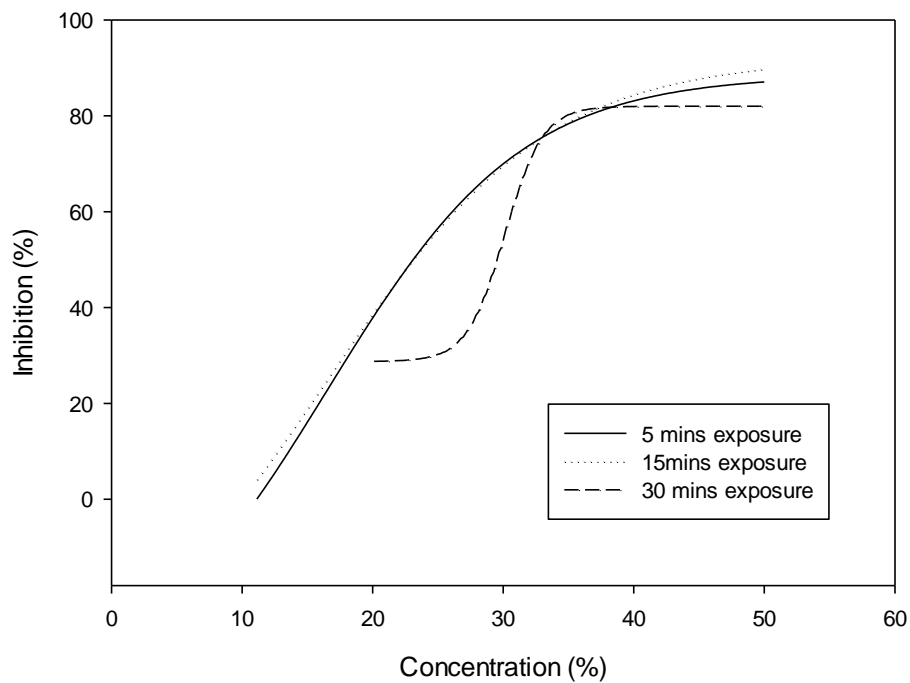
B25L 14 days

Figure 5.6 : Relation of 25% slag containing block leachate concentration vs inhibition.

B50L 14 days

Figure 5.7 : Relation of 50% slag containing block leachate concentration vs inhibition.

B75L 14 days

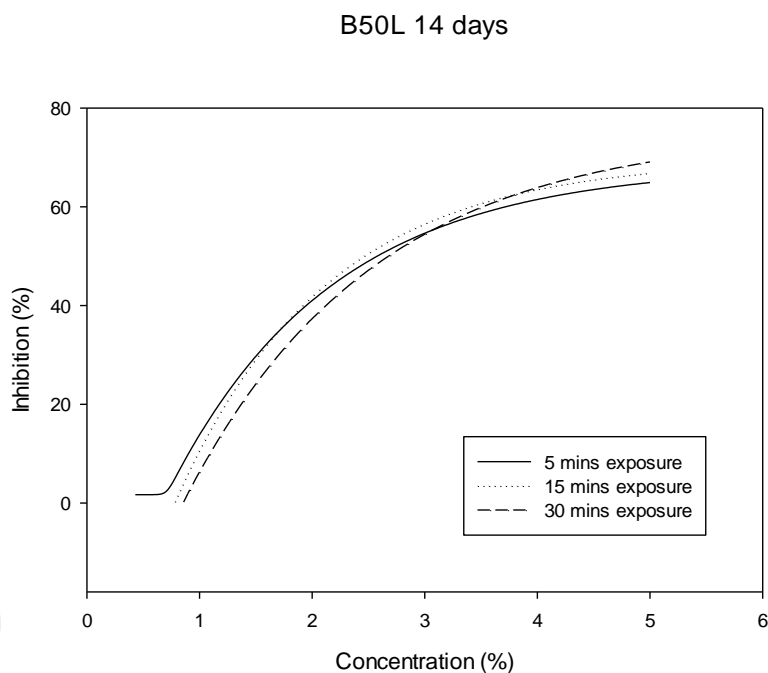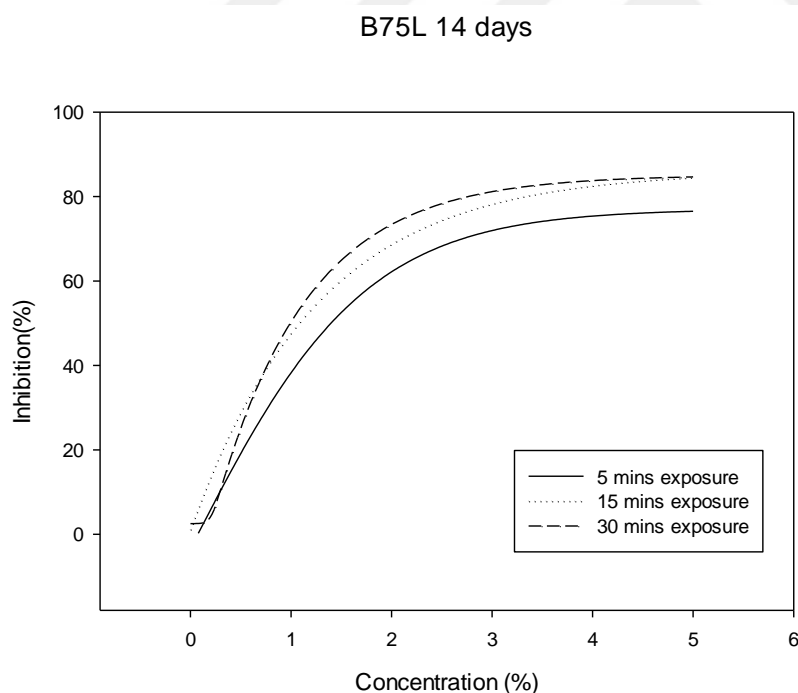**Figure 5.8 :** Relation of 75% slag containing block leachate concentration vs inhibition.

In Figure 5.9 and 5.10 comparisons of EC50 and TU values are interpreted. According to those bar charts, stabilization/solidification decreases the toxicity of slag significantly. 25% slag containing block leachate toxicity is in the same range of

toxicity units of control block leachate and it is very less than raw slag leachates. So S/S aplication is appropriate for the slag ratio in blocks under 25%.
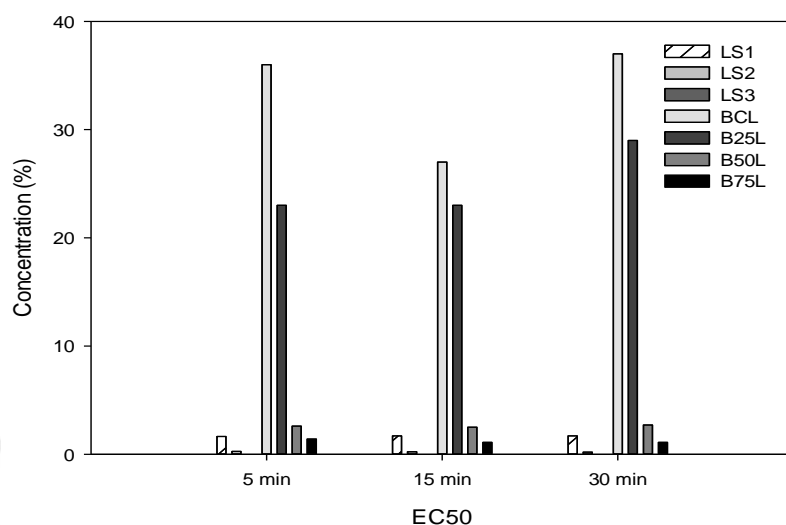

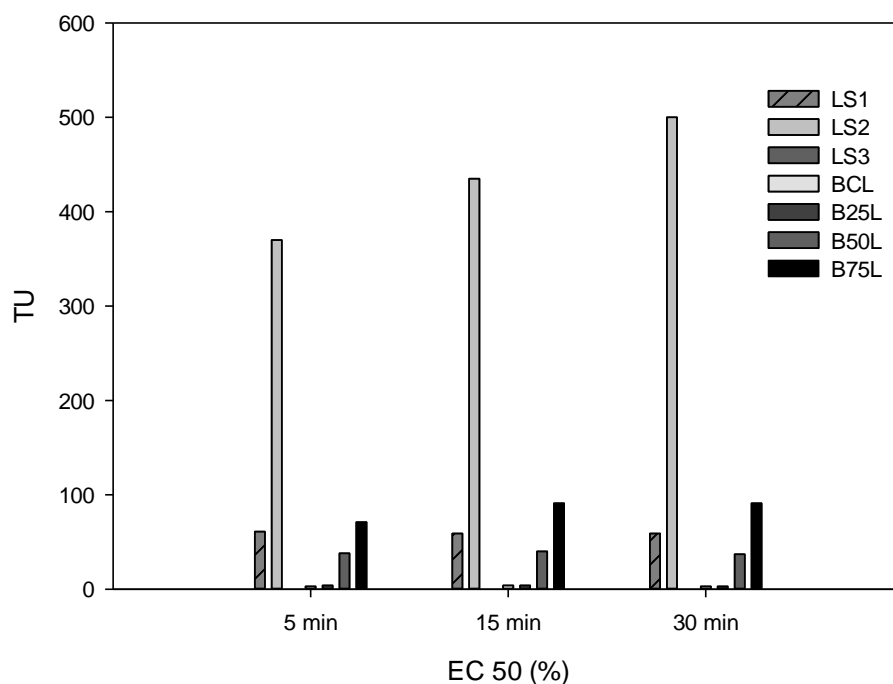**Figure 5.9 :** Comparison of EC50 values of different leachates.

Figure 5.10 : Comparison of TU values of different leachates.

Also a toxicity comparison is done with the synthetic samples containing lead and other metals under the minimum toxic concentration and LDR limits. EC_{50} values were found to be higher than 100 which is not toxic in terms of toxicity unit of "1".

5.3 Metals Precipitation in Slag Leachates by Coagulation / Flocculation

Mixed slag leachates are prepared with same volumes of leachs of pH 2,88 and pH4,93 samples and replicates. A jar test was run for one minute rapid mixing over 200 rpm, whilst initial pH was 4,70, optimum pH values were determined 9,5 and 9,3 for NaOH and lime coagulant respectively. Jar test operations are as follows:

1. Jar test for NaOH coagulant

   1 minute rapid mixing, 200 rpm, 15 minute slow mixing, 20 rpm

   Optimum coagulant dosage 1600 mg/L, coagulant aids: 1 mL cationic polyelectrolyte

   Initial pH 4,70, optimum pH 9,5, sludge volume %20 v/v

2. Jar test for lime coagulant

   1 minute rapid mixing, 200 rpm, 15 minute slow mixing, 20 rpm

   Optimum coagulant dosage 1600 mg/L, coagulant aids: 1 mL cationic polyelectrolyte

   Initial pH 4,70, optimum pH 9,3, sludge volume %20 v/v

Aforementioned jar test results are given in Table 5.6.

Table 5.6 : Jar test performance for combined slag leachates in various periods.

Samples	Pb (mg/L)	Fe (mg/L)	Mn (mg/L)	Zn (mg/L)	Cd (mg/L)	Ni (mg/L)	Cu (mg/L)
Leachate in jar test with NaOH	42,28	10300	<0,1	15,1	<0,05	<0,3	<0,3
Leachate in jar test with lime	42	9400	<0,1	16,5	<0,05	<0,3	<0,3
Supernatant of test w/ NaOH	<1	<0,3	<0,1	1,35	<0,05	<0,3	<0,3
Supernatant of test w/ lime	<1	<0,3	<0,1	1,49	<0,05	<0,3	<0,3

Jar test results enable us to conclude that removal efficiency of heavy metals from leachates were very high and also to calculate about the feeding the sludge back to the furnace. Feedback of the sludge was considered as metals recovery and calculated as given in Figure 5.11.
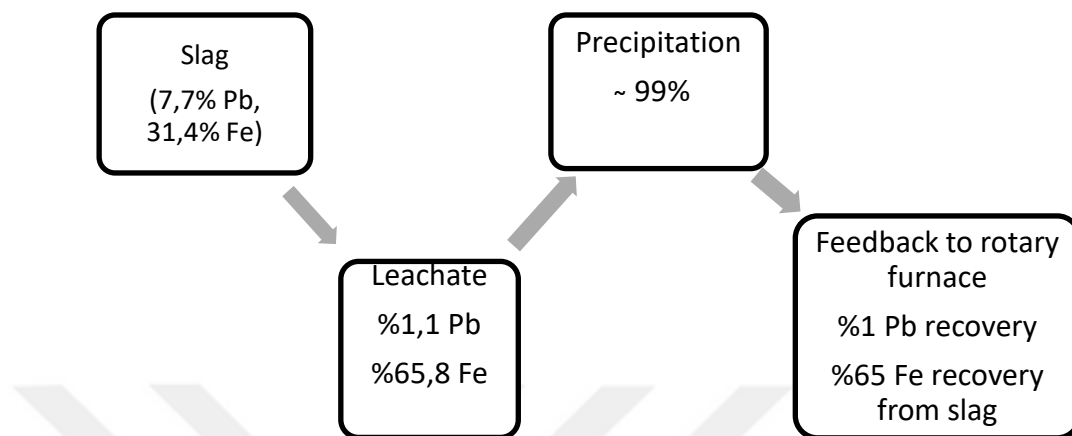

Figure 5.11 : Calculations of metals recovery from slag.

Abbreviations for all of the test samples are given in Table 5.6. Those are used for signing.

Table 5.7 : Abbreviations and definitions of test samples.

Abbreviation	Sample definition
LS$_1$	Raw slag leachate in pH 4,93
LS$_2$	Raw slag leachate in pH 2,88
LS$_3$	Raw slag leachate in pH 7,0
BCL	Control block leachate
B25L	25 % slag containing block leachate
B50L	50 % slag containing block leachate
B75L	75 % slag containing block leachate

6. CONCLUSION AND RECOMMENDATION

From the results obtained by experimental sets, are interpreted as follows:

- Slag from secondary lead production industry is designated as hazardous waste according to TCLP but not hazardous according to DIN 38414-4,

- It is concluded that 2,88 and 4,93 pH values of leach procedures are the key factors playing the important role for metal leaching both for raw and S/S performed slag.

- However when leach procedure is performed at 7 pH, leachates do not show any toxicity nor for raw slag and neither for S/S performed slag. Acidic leachates show toxicity according to high solubility levels of heavy metals.

- Toxicity tests on S/S products show that the only ratios of 25% slag in blocks by volume is successful for detoxification of slag. S/S performance does not show any difference by the difference in mechanic properties improvement period. After both 14 and 28 days improvement periods, block samples did not show any difference in toxicity and metal leaching.

- Two options are recommended for management of the slag. First, as slag is not suitable for directly landfilling, S/S products of slag are send to landfill according to land disposal restrictions and second, slag can be leached in acetic acid or acid solution from battery bulk in a 20 times the weight of slag in WWTS at pH 4,7 and after 1 day, metals are precipitated by lime addition. 65% of iron and 1% lead recovery is obtained from slag after this operation by feeding the sludge to the rotary furnace. It is recommended thar for the remaining slag after leaching process can be directed to S/S process and then landfill. Second option is shown in a flowchart in Figure 5.11.

- Further studies are recommended for economical comparison of the two options above.

Finally, it must be stressed that low pH values of leach procedures even using acetic acid are the most important factors of metal leaching. The lower the pH is, the higher the solubility of metals. Both for toxicity and solubility low pH is the limiting factor. In conclusion, leaching behavior should also be evaluated at pH 7 and reflected to the standards. Environmental simulation of leach procedures is the most important factor for a toxicity evaluation. Further studies can be done by continuous extraction techniques.

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