## HAZARDOUS WASTE INVENTORY OF TURKEY

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BY

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## ABSTRACT

### HAZARDOUS WASTE INVENTORY OF TURKEY

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In this study, hazardous waste inventory for Turkey is developed based on wastes identified as hazardous in European Waste Catalogue and Regulation on Control of Hazardous Wastes, Annex 7 Necessity of such inventory arises from importance of acquiring information on the amount of hazardous wastes generated and on their countrywide distribution for a sound hazardous waste management system for Turkey. Hazardous waste inventory is constructed by using waste generation factors obtained from literature which are coefficients that relate production with environmental emissions. Whenever possible, direct information obtained from generators was utilized. Both absolute and minor entries are covered.

It is estimated that 4,940,000 - 5,110,000 t/yr of hazardous wastes are being generated in Turkey. 1,790,000 - 2,252,000 t/yr of these are classified as absolute entries and 3,146,000 - 3,160,000 t/yr of hazardous wastes are minor entries.

It is observed that highest generation occurs from mining and thermal processes which involve high amounts of minor entries. Beside these industries highest generation occurs from wood preservation. Per capita hazardous waste generation is estimated as 30 - 77 kg/capita/yr which is in accordance with per capita generation range of EU.

Highest hazardous waste generation occurs from Marmara Region with 527,730 t/yr followed by Aegean (524,580 t/yr), Central Anatolia (481,820 t/yr), Black Sea Region (277,850 t/yr), Mediterranean (211,580 t/yr), Southeast Anatolia (58,290 t/yr) and Eastern Anatolia (36,520 t/yr) excluding minor entries from mining industry and thermal processes. The trends in hazardous waste generation and GDP from manufacturing industry show the same trend. Contribution of regions are in the same order both in hazardous waste generation and GDP.

Keywords: hazardous waste, European Waste Catalogue, waste management, inventory, waste generation factors

## ÖZ

## TÜRKİYE'NİN TEHLİKELİ ATIK ENVANTERİ

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Bu çalışmada Avrupa Atık Kataloğu (AAK) ve Tehlikeli Atıkların Kontrolü Yönetmeliği (TAKY) Ek7'de yer alan atıklar sınıflandırmasını temel alarak Türkiye için tehlikeli atık envanteri oluşturulmuştur. Böyle bir envanterin gerekliliği tehlikeli atık miktarlarının ve Türkiye çapında dağılımının etkin bir tehlikeli atık yönetim sistemi için teşkil ettiği önemden kaynaklanmaktadır. Tehlikeli atık envanteri, üretim süreçlerinin girdilerini, üretilen atıklarla ilişkilendiren atık üretim faktörleri literatürden alınarak oluşturulmuştur. Mümkün olduğu durumlarda atık üreticilerinden doğrudan bilgi alınmıştır. AAK ve TAKY Ek7'de verilen tüm atıklar kapsanmıştır.

Bu çalışmanın sonucunda yılda 4.940.000 – 5.110.000 ton arası tehlikeli atık ortaya çıktığı bulunmuştur. Bu miktarın 1.790.000 – 2.252.000 arası "Absolute Entry" olarak listelenen, 3.146.000 – 3.160.000 ton/yıl arası "Minor Entry" olarak listelenen atıklardan meydana gelmektedir.

En yüksek üretimin, yüksek miktarda "Minor Entry" oluşturan madencilik sektörü ve ısıl işlemlerden kaynaklandığı gözlenmiştir. Bu endüstriler dışında en

yüksek tehlikeli atık üretimi emprenye sanayinden kaynaklanmaktadır. Kişi başına düşen tehlikeli atık üretimi 30 – 77 kg/yıl/kişi olarak hesaplanmıştır ve AB için verilen kişi başına düşen tehlikeli atık miktarı aralığı ile uyumludur.

Madencilik sektörü ve ısıl işlemlerden kaynaklanan "Minor Entries" göz ardı edildiğinde en yüksek tehlikeli atık üretimi 527,730 ton/yıl ile Marmara Bölgesi'nde gerçekleşmektedir. Marmara Bölgesini sırasıyla, Ege (524,580 t/yıl), İç Anadolu (481,820 ton/yıl), Karadeniz (277,850 ton/yıl), Akdeniz (211,580 ton/yıl), Güneydoğu Anadolu (58,290 ton/yıl) ve Doğu Anadolu (36,520 ton/yıl) bölgeleri izlemektedir. Tehlikeli atık üretimi ve üretim sanayinden kaynaklanan GSYİH eğilimleri uyumludur. Bölgelerin atık üretimi ve üretim sanayinden kaynaklanan GSYİH' ya katkıların aynı sıradadır.

Anahtar Kelimeler: Tehlikeli atık, Avrupa Atık Listesi, atık yönetimi, envanter, atık üretim faktörleri

To mum and dad

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#### ABBREVIATIONS

EU : European Union TAKY : Tehlikeli Atıkların Kontrolü Yönetmeliği RCWO: Regulation on Control of Waste Oils RCPW : Regulation on the Control of Packaging and Packaging Waste RCWBA: Regulation on Control of Waste Batteries and Accumulators IPPC : Integrated Pollution Prevention and Control BAT : Best Available Techniques EWC : European Waste Catalogue RCHW: Regulation on Control of Hazardous Wastes EPER : European Pollutant Emission Register MoEF : Ministry of Environment and Forest SIS : State Institute for Statistics WDF : Waste Declaration Form BREF : Best available techniques reference document TWG : Technical working group HWL : Hazardous Waste List EPIS : Environmental Pressure Information Systems KBİ : Karadeniz Bakır İşletmeleri **USEPA:** United States Environmental Protection Agency TOBB : Union of chambers and Commocity of Exchanges **BDAT** : Best Demonstrated Available Technology TÜPRAŞ: Türkiye Petrol Rafinerileri A.Ş. ATAŞ : Anadolu Tasfiyehanesi A.Ş. TÜGSAŞ: Türkiye Gübre Sanayi A.Ş. GDP : Gross domestic product mfsu : manufacture, formulation, supply and use DNT : Dinitrotoluene

- TNT: Trinitrotoluene
- LDPE : Low density polyethylene
- HDPE : High density polyethylene

- VCM : Vinyl chloride monomer
- PVC : Polyvinyl chloride
- PP : Polypropylene
- FGD : Flue gas desulphurization
- CO : Carbon monoxide
- PM : Particulate matter
- VOC : Volatile organic compounds
- CCPS : coal combustion products
- SPL : Spent Pot Lining
- TEİAŞ : Türkiye Elektrik İletim A.Ş.
- PCB : Printed Circuit Boards

## **CHAPTER 1**

## **INTRODUCTION**

#### 1.1 Definition of Hazardous Wastes

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

- 1. such wastes are nondegradable or persistent in nature,
- 2. they can be biologically magnified,
- 3. they can be lethal, or
- 4. they may otherwise cause or tend to cause detrimental cumulative effects [1]. Properties of wastes which render them hazardous are given in Table 1. 1.

	Property	Comment				
		Substances and preparations which may explode under the				
H1	Explosive	effect of flame or which are more sensitive to shocks or				
		friction than dinitrobenzene				
		Substances and preparations which exhibit highly				
H2	Oxidizing	exothermic reactions when in contact with other				
		substances, particularly flammable substances.				
НЗ-А		- Liquid substances and preparations having a flash point				
	Highly flammable	below 21°C (including extremely flammable liquids), or				
		- Substances and preparations which may become hot and				
		finally catch fire in contact with air at ambient temperature				
		without any application of energy, or				
		- Solid substances and preparations which may readily				
		catch fire after brief contact with a source of ignition and				
		which continue to burn or to be consumed after removal of				
		the source of ignition, or				
		- Gaseous substances and preparations which are				
		flammable in air at normal pressure, or				
		- Substances and preparations which, in contact with water				
		or damp air, evolve highly flammable gases in dangerous				
		quantities.				

Table 1. 1: Properties o	f hazardous wastes [2]
--------------------------	------------------------

	Property	Comment					
H3-B	Flammable	Liquid substances and preparations having a flash point equal to or greater than 21°C and less than or equal to 55°C.					
H4	Irritant	Non-corrosive substances and preparations which, through immediate, prolonged or repeated contact with the skin or mucous membrane, can cause inflammation.					
Н5	Harmful	Substances and preparations which, if they are inhaled or ingested or if they penetrate the skin, may involve limited health risks.					
H6	Toxic	Substances and preparations (including very toxic substances and preparations) which, if they are inhaled or ingested or if they penetrate the skin, may involve serious, acute or chronic health risks and even death.					
H7	Carcinogenic	Substances and preparations which, if they are inhaled or ingested or if they penetrate the skin, may induce cancer or increase its incidence.					
H8	Corrosive	Substances and preparations which may destroy living tissue on contacts.					
Н9	Infectious	Substances containing viable micro-organisms or their toxins which are known or reliably believed to cause disease in man or other living organisms.					
H10	Teratogenic	Substances and preparations which, if they are inhaled or ingested or if they penetrate the skin, may induce non- hereditary congenital malformations or increase their incidence.					
H11	Mutagenic	Substances and preparations which, if they are inhaled or ingested or if they penetrate the skin, may induce hereditary genetic defects or increase their incidence.					
H12		Substances and preparations which release toxic or very toxic gases in contact with water, air or an acid					
H13		Substances and preparations capable by any means, after disposal, of yielding another substance, e.g. a leachate, which possesses any of the characteristics listed above.					
H14	Ecotoxic	Substances and preparations which present or may present immediate or delayed risks for one or more sectors of the environment.					

Table 1. 1 continued [2]

The above mentioned properties of hazardous wastes necessitate strict control and regulation of these wastes. Legal framework for hazardous wastes is obviously the most important means of regulation of hazardous wastes. At both national level, and European level, there are a number of regulations and directives that define the proper management of hazardous wastes.

#### 1.2 Legislative Framework Regarding Hazardous Wastes

Regulation on Control of Hazardous Wastes (RCHW) of Turkey is the most important national regulation covering issues about hazardous wastes. It comprises articles regarding prevention of disposal of hazardous wastes to receiving bodies without any treatment, control over generation and transportation, prevention of export of hazardous waste and control of their regulation, minimization of hazardous waste generation at the source, in cases where generation cannot be avoided disposal of hazardous wastes to a location most close to the generation points, foundation of disposal facilities and their control and issues regarding management of these wastes [3].

In addition to this core regulation, there are some other legal arrangements that are related with the hazardous wastes such as Regulation on Control of Waste Oils (RCWO), Regulation on the Control of Packaging and Packaging Waste (RCPW), Regulation on Control of Waste Batteries and Accumulators (RCWBA), Regulation on Incineration [4]. The RCWO regulates the collection, reuse, recycling and disposal of waste oils which are defined as hazardous wastes in the RCHW. The RCPW regulates the production, disposal, packaging waste minimization, recycling and reuse institutional and technical standards related to packaging materials and packaging wastes. The RCWBA regulate the issues about batteries and accumulator beginning from production to final disposal and import of these items.

At European level the most important directives related to hazardous wastes are European Union (EU) Council Directive of 15 July 1975 on waste (75/442/EEC) and Council Directive of 12 December 1991 on hazardous waste (91/689/EEC). Council Directive 75/442/EEC comprises articles about waste hierarchy, risk prevention, a network of disposal installations; establishment of a competent authority, waste management plans, obligations of waste holder, permits, inspection, record keeping and polluter pays principle [5]. On the other hand, Council Directive 91/689/EEC comprises articles regarding description of hazardous wastes, mixing of hazardous wastes with other hazardous wastes and non-hazardous wastes, permits, collection, transport and temporary storage [2]. Annexes of Council Directive 91/689/EEC includes categories or generic types of hazardous waste listed according to their nature or the activity

which generated them, constituents of the wastes which render them hazardous when they have properties described, and properties of hazardous wastes in Table 1.1 [2].

Another EU legislation related with hazardous wastes is the Council Directive numbered 96/61/EC of 24 September 1996. This directive, entitled as integrated pollution prevention and control (IPPC Directive), requires an integrated approach to reduce pollution and take action concerning the prevention and control of pollution from industrial plants. According to the IPPC directive, emission limit values, parameters or equivalent technical measures should be based on the **best available techniques (BAT)** [6]. Another important aspect of IPPC Directive is establishment of an inventory of principal emissions and sources responsible that may be regarded as an important instrument making it possible in particular to compare pollution activities in the Community [6].

Turkey is in a period of adopting EU directives as it is recognized as an EU candidate country in December 1999. In December 2004, EU defined the conditions for the opening of accession negotiations [7]. From that day on, harmonization studies related to EU directives gained impetus. As noted in the Turkey's Progress Reports, in the way to the EU membership, efforts are needed in the area of waste management to secure solid investments in the medium term. One of the major issues in the area of waste management that require investments is the hazardous wastes sector that is regulated by the the EU's Directive on Hazardous Waste (91/689/EEC). The key requirement of this Directive is establishment of a sound management system to cope with problems originated due to these wastes. For establishment of such a system, it is essential to acquire information on the amount of hazardous wastes generated and their countrywide distribution.

According to estimates by ENVEST Planners, Turkey needs to invest about EUR 40-50 billion in the environmental sector in order to meet the requirements of the EU environmental directives [8]. This high investment value underlines the absence of past investments and a necessity of a sound environmental management system for Turkey. An important part of environmental management system is planning towards management of wastes.

Currently, not only on hazardous wastes but also on non-hazardous wastes no satisfactory management practice exist, although, there is a legislative framework regarding environmental issues and in time more regulations in environmental issues will be adopted from EU. However, enforcement of these regulations and legislations cannot be realized unless a sound environmental management system is put into action. The first step of such an environmental management system is the scope of the system. For a hazardous waste management system, this means determination of the generators and their locations and the amount of hazardous wastes generated. After completion of this phase, characterization of these wastes shall follow. As the characteristics of different waste streams are known along with their origin and amounts, different options for various steps of management system can be determined.

#### 1.3 Objective and Scope of the Study

It is obvious that a hazardous waste inventory study as a preliminary step for a sound hazardous waste management plan is required in Turkey. This is due to the fact that planning, which is the first step in every waste management plan cannot be accomplished properly without information on the amount of hazardous wastes generated in the country.

The objective of the present study is to develop a hazardous waste inventory for Turkey. This inventory study is based on a detailed evaluation of hazardous waste generating activities in Turkey; their locations, processes (when needed), and the production capacities. Estimations are conducted by using or developing some coefficients that related to production of wastes so called **waste generation factors** as a basis. These factors, as described in Chapter 3, relate waste generation to waste generation to consumption of raw materials or products. Even in European countries such as France and Spain, determination of hazardous waste generation is accomplished through estimations [9].

During the study, waste categorization given in the European Waste Catalogue (EWC) and Annex 7 of RCHW of Turkey were adopted. (Information about EWC and Annex 7 of the RCHW of Turkey is covered in more detail in Section 2.3).

Besides estimating the amount of hazardous waste generated, another aim of this study is to develop a systematic way of hazardous waste generation estimation whose validity can be maintained even when industrial capacities change. Since waste factors developed for specific processes will not differ from time to time; to update the amount of hazardous waste generation it would be sufficient to use new capacities instead of former ones in calculations. Therefore, such an estimation methodology developed hazardous waste inventory would have the opportunity of being updated as industrial capacities change.

#### **CHAPTER 2**

## **BACKGROUND INFORMATION**

#### 2.1 Situation in European Union

As a requirement given in IPPC Directive, in European Union well documented studies regarding determination of waste generation amounts have been conducted [6].

In IPPC Directive, establishment of an inventory of principal emissions and sources is emphasized [6]. In July 2000, the European Commission adopted a Decision on the implementation of a **European Pollutant Emission Register** (EPER) according to Article 15 of Council Directive 96/61/EC concerning IPPC [10]. National governments of all EC Member States are required to maintain inventories of emission data from specified industrial sources and to report emissions from individual facilities to the European Commission. The reported data will be made accessible in a public register (EPER), which is intended to provide environmental information on major industrial activities [10].

Besides this database, there are studies involving estimation of hazardous waste generated in European Union. In a representative study conducted by Brodersen et al. (2002), a questionnaire was sent to countries in August 1999 seeking information about:

- o hazardous waste generation classified according to the EWC at two-digit level;
- o the 20 largest waste types classified according to the EWC;
- o the relationship between the national waste classification codes and the EWC;
- hazardous waste generation classified according to economic activity (NACE codes);

o General questions on hazardous waste generation and data collection [9].

In the report of this study, countries which use one set of sources of information for all sectors are given. Among them Ireland use information from producers, Brussels, Ireland and Wallonia use information from collectors, Austria, Denmark, Ireland and Wallonia use information from treatment/disposal facilities and Germany use information from competent authorities. An important source of information given in this document is estimates which are used by France and Spain [9].

Results related to hazardous waste generation amounts are also presented in this report. These results are given in Table 2. 1.

Table 2. 1. Hazardous waste generation in Europe (1,000 tons) [5]									
Country	1990	1991	1992	1993	1994	1995	1996	1997	1998
Austria				499	513	577	606		
Belgium									
Brussels									
Belgium					1,033	1,079	1,410	1,625	
Flanders					1,035	1,079	1,410	1,025	
Belgium						419	427	470	475
Wallonia						419	427	470	475
Denmark					194	247	264	249	281
Finland			559					481	
France	7,000						9,000		
Germany	13,079			9,093					
Greece	450		450			350			287
Iceland				4.9	5.7	4.3	5.7	5.8	6.8
Ireland	66		99			248	230		
Italy	3,246	3,387				2,708		3,401	
Luxembourg	116			861	811	197	157	142	
Netherlands	1,040		1,430	836	890	868	959	1,271	
Norway	60			98	92	102	119	128	141
Portugal						668		595	
Spain	1,700				3,394				
Sweden				394					
United			2 452	2 077					
Kingdom			2,452	2,077					

 Table 2. 1: Hazardous waste generation in Europe (1,000 tons) [9]

The data show increasing quantities of hazardous waste during the 1990s for Austria, Belgium, Denmark, Iceland, Ireland, Italy, Luxembourg, the Netherlands, Norway and Spain, with a decrease in quantities in Finland, Germany, Greece, Portugal and the United Kingdom. However, the trend is not very clear due to the fact that the amounts of hazardous waste in some countries fluctuate from year to year. Furthermore, some countries do not have access to new data, which makes it difficult to establish reliable trends in relation to the generation of hazardous waste [9]. Increasing quantities of hazardous waste can be the result of better collection of information and registration of waste, and not necessarily the result of a real increase in waste generation [9].

16% of hazardous wastes are originating from *organic chemical processes*. Other important sources are *inorganic wastes from thermal processes* (13%), *inorganic waste with metals from metal treatment and the coating of metals; non-ferrous hydrometallurgy* (13%), *inorganic chemical processes* (10%) *oil wastes and other liquids* (10%) and *wastes from waste treatment facilities* (8%). The rest of the sources are all of minor importance. It is interesting to note that waste from households is only about 1% of the total hazardous waste quantities [9]. Besides these findings, results at 6-digit level are also obtained.

In addition to general waste inventory studies, report about specific waste streams are also published [11]. In one of these studies yearly generation of selected waste streams are presented for EU member states [11].

These studies are important in that they give quantitative results regarding hazardous waste production in Europe. Moreover, they are examples of detailed waste inventory studies.

## 2.2 Situation in Turkey

There are very limited data on hazardous waste generation in Turkey. Major sources of information on hazardous wastes are Manufacturing Industry Survey developed by the State Institute of Statistics (SIS) on a regular basis, data from Ministry of Environment and Forestry (MoEF), and the project entitled "Hazardous Wastes Management" realized by TCT-Zinerji Consortium for the Ministry of Environment and Forestry [12, 13].

Manufacturing Industry Survey of SIS includes air pollution statistics, municipal wastewater statistics, municipal solid waste statistics, municipal drinking water statistics, mining industry waste statistics, and wastes statistics of industrial districts' [14]. According to this survey, the total quantity of hazardous waste generated in Turkey (from 331 establishments) in 2000 is about 1.3 million tons/year. The data from the survey conducted by SIS covered only part of provinces and waste generating industries, and it is highly probable that the actual hazardous waste generation is substantially higher than reported. Findings of this statistic are not adequate to present a waste inventory for industrial wastes because industrial wastes comprise only a portion of the results given under Manufacturing Industry Survey at the website of SIS. Nevertheless, these statistics are continuously being updated and there is a possibility that statistics covering new topics more related to industrial wastes will be added.

In Hazardous Waste Management Project, hazardous waste generation and disposal practices, institutional structure and legal framework are covered and possible sources of problems are investigated. Suggestions were made on legal framework related to management of hazardous wastes and harmonization with EU directives [12].

In Hazardous Waste Management Project, the hazardous waste generation in Turkey was evaluated based on the total number of employees working in hazardous waste generating industries adopting a method from Germany. The hazardous waste generation estimation was made for the regions of Marmara, Aegean and Mediterranean considering the industrial development in these regions. The hazardous waste generation rates predicted for the years 2000 and 2020 by this project are shown in Table 2. 2 [12]

	Hazardous waste generation, tons/year							
Year	Landfillable	Burnable	Municipal	TOTAL				
2000	1 067 400	118 600	24 890	1 210 890				
2020	1 748 700	194 300	40 870	1 983 870				

Table 2. 2: Hazardous Waste Generation Estimated in the Project by TCT-Zinerji. [12]

Another means of data collection about hazardous waste generation is waste declaration forms submitted to the local branches of the MoEF by the waste generators according to the requirement of the RCHW.

A discussion about waste declaration forms is included in Hazardous Wastes Management Project Final Report. For the evaluation of current status waste declaration forms are considered and it is concluded that information about hazardous waste generation is not being collected properly by using waste declaration forms [12]. Hazardous Waste Management Project Final Report pointed out the main obstacles encountered in current hazardous waste reporting system which fully depends on waste declaration forms filled by hazardous waste generators. Among these obstacles there
are confusion of waste generators over how to in waste declaration forms (WDFs), unwillingness of generators to fill the waste declaration forms and unawareness of generators about their producing wastes that are hazardous [12]. According to the Article 9 of the RCHW, waste generators are obliged to submit "waste declaration forms" to the local branches of the MoEF on a yearly basis. As learned from the MoEF, the total number of establishments submitting WDFs is approximately 1000; while the total number of waste generators is predicted to be over 10,000. According to the data collected by the SIS by the Manufacturing Industry Survey; the number of manufacturing industry establishments employing more than 25 workers is 7480 (1999 data). Therefore, the percentage of establishments submitting WDFs is not representative. Another indicates that the information collected via these WDFs is not representative. Another indication for the unreliability of the information in WDFs is the high variation observed in the number of WDFs submitted to the Ministry in different years as given in Table 2. 3 [13].

 Year

 1995
 1996
 1997
 1998
 1999

 806
 1395
 501
 479
 472

Table 2. 3: Number of WDF Submitted to the MoEF [13]

This situation reveals the need for other means to gather data concerning hazardous waste generation. The report underlines the necessity of a reliable waste inventory and suggests empirical calculations that could be made by using waste generation factors as an option [12].

Technical Assistance for Environmental Heavy-Cost Investment Planning, Turkey - Directive Specific Investment Plan for Council Directive on Hazardous Waste (91/689EEC) Report covers the investment planning for Council Directive on Hazardous Waste (91/689EEC). The report discusses the present situation in Turkey regarding this issue in terms of legal framework, institutional set-up and most importantly hazardous waste generation and management.

#### 2.3 Reference Documents

In this section, reference documents that are helpful in estimation of hazardous waste generation are summarized.

As it was stated in Section 1.2, according to IPPC directive, emission limit values, parameters or equivalent technical measures should be based on the best available techniques. BAT are required to be considered (under IPPC directive) in order to avoid or reduce emissions resulting from certain installations and to reduce the impact on the environment as a whole [15].

The European IPPC Bureau functions to gather technical information on best available techniques under the IPPC Directive and to create reference documents (BREFs) which must be taken into account when the competent authorities of Member States determine conditions for IPPC permits. Each sector of industry to be covered by the IPPC directive will be addressed by a specific Technical Working Group (TWG) comprising nominated experts from Member States, EFTA countries, Accession countries, industry and environmental NGOs [16]. Best available techniques reference documents (BREFs) prepared by TWGs or still in progress include 33 topics [17]. These reference documents are constantly being revised after completion by TWGs.

In the content of BREFs first of all an executive summary in which the main findings from all chapters of the document are presented. After general information is given for that specific industry or topic in applied processes and techniques chapter briefly describes the production processes and techniques currently applied in the industrial sector covered by the BREF. This chapter includes information about raw and auxiliary materials used, material processing, product manufacture and finishing, handling of products, by-products and residuals. Another chapter named current consumption and emission levels follow in which range of currently observed emission and consumption levels for the overall process and its sub-processes are given. In this chapter waste generation factors for industry in question are presented if there is any [18].

In techniques to consider in determination of BAT a catalogue of emission reduction or other environmentally beneficial techniques that are considered to be most relevant in the determination of BAT (both generally and in specific cases) are provided. Information given on these techniques include description and environmental benefits of the techniques as well as operational data, cross media effects, applicability, economics, driving force for implementation [18].

In following BAT chapter, with standard explanatory introduction, conclusion on what is considered to be BAT in a general sense for the sector based upon the information in the previous chapter is presented. BREF is generally concluded with emerging techniques chapter in which any novel pollution prevention and control techniques that are reported to be under development and may provide future cost or environmental benefits are identified and concluding remarks chapter [18].

Other main references for the thesis are EWC and RCHW. The creation of the EWC and Hazardous Waste List (HWL) represents the most significant move to date towards harmonization of information on waste production and management in Europe and the development of a common Europe-wide waste classification system for hazardous and non-hazardous waste [9].

The EWC was established in December 1993 by Council Decision 94/3/EC and included at that time 645 waste types. The HWL was subsequently established in December 1994 by Council Decision 94/904/EC. The HWL is a subset of the EWC and consisted of 236 of the 645 EWC waste types, which were considered by the EU to be hazardous at the time that the list was agreed [9].

In general, the EWC and HWL are source and process-based listings of wastes. The EWC has three levels:

- 1. The highest level with 20 entries (two-digit codes) often describing the source and the branch generating the waste;
- Each of the 20 main group has several subgroups (four-digit codes) often describing the process generating the waste;
- 3. Each subgroup has several waste codes (six-digit codes) describing the substances in waste. The HWL is defined on this level [9].

Entries that present hazardous wastes are marked with an asterisk in EWC [19].

In addition to levels of entries another major categorization in EWC is absolute and minor entries. Absolute entries are described as hazardous wastes regardless of any threshold concentrations and minor entries are described as are wastes that are hazardous only if dangerous substances are present above threshold concentrations [19].

EWC is implemented in RCHW of Turkey to be effective after March 14 2005.

# **CHAPTER 3**

# METHODOLOGY

It is obvious that the best way of developing a waste inventory is the collection of waste generation data from the waste generators. However, unfortunately when it comes to wastes, generators are unwilling to reveal the amount of wastes generated. This situation is worse in the case of hazardous wastes as discussed in Chapter 2. In occasions where waste declaration systems relying on producers do not work properly theoretical methods can be regarded as important alternative.

#### 3.1 Waste Generation Factors

In this section, information about waste generation factors is given.

The Environmental Pressure Information Systems (EPIS) project in Eurostat which is acknowledged as a new tool for statistics on material flows and pollution releases, started as a part of the Commission's initiatives related to the Commission's Communication to the Parliament on Environmental Indicators and Green National Accounting (COM(94) 670) in 1994. The earlier experiences in the German Statistische Bundesamt provided a promising start for the European project [19].

The objective of Eurostat's Environmental Pressure Information System (EPIS) is to provide a tool for the compilation and modeling of timely data on environmental pressures arising from different economic activities [19].

EPIS leans on a conventional material balance approach; the quantities of inputs of materials to one process are in balance with the system accumulation and products and residuals in a given period [19]. Material balance approach used in EPIS is given in Table 3. 1.

Inputs		Outputs
Feedstocks		Products
Operating substances	PROCESS	Residues
Energy	1100105	Air emissions
Water		Wastewater
Air		Waste

Table 3. 1: Material balance of a process [19]

EPIS involves compilation of a technical database involving coefficients for inputs (feedstocks, operating substances, energy, air and water) and outputs (products, air, waste water and waste) for the majority of the selected high pressure processes. The core of EPIS is a matrix of 100-150 high-pressure processes in Europe, selected by an expert group. The prioritization of processes is done on the basis of the estimated pressures: if at least one type of pressure resulting from all processes of the same type is quantitatively remarkable (more than 5% or only more than 1% of the national total), it will be included in the high pressure processes [19].

Environmental factors are in general related to an activity or source, e.g. describing emissions linked to an industrial process. They are obtained by relating the quantity emitted to a specific product or source or activity. These factors are based on measured and/or calculated and/or estimated values [21].

At national level waste factors as an informative tool may help to integrate environmental data with economic aspects, to describe for instance the quantity of waste per GDP unit or per inhabitant. Thus they might serve as a tool in order to compare efficiency of regions in minimizing waste generation. The typical customer of these factors could be European Parliament or the European Commission, in order to check where financial resources could support national or regional attempts towards less waste. On the macro-economic level, waste factors will also supplement national or regional waste statistics and can therefore be used by statistics offices. They can be used to support the authorities in drawing up their national or regional waste management plans. Waste factors at national level offer also the possibility to compare the waste situation between Turkey and EU and other industrialized regions in the world, with the aim to improve waste management. [21].

In order to improve material efficiency at industrial sector level, waste factors could consider the amount of waste as a whole, or specified on type of fuel or related to the product [21].

At enterprise level or production site level management faces more and more the challenge of implementing an Environmental Management and Auditing System and of paying more attention to the 'productivity' in waste. There is an increasing need for factors that can be applied as tools for the source oriented 'plan-do-check-act' approach in waste management, and which are therefore indispensable parts of an ecocontrolling system [21].

#### 3.2 Estimation of Hazardous Waste Generation

In this thesis, hazardous waste generation factors are used in order to calculate hazardous wastes produced from different industrial applications and from other sources such as municipal origin. As stated in Section 1.3, categorization given in EWC and Annex 7 of RCHW is adopted. Absolute entries are mainly covered. Calculations on minor entries are made whenever data is available in terms of both waste generation factors and industrial capacities.

Throughout the research for each 2-digit entry, as a first step, production capacities in Turkey related to that specific entry is gathered. An important part of the research is to acquire information about industrial capacities. For capacity information, 8. Five Year Development Plan Commission Reports and The Supreme Audit Board of Prime Ministry reports were used. Whenever data could not be gathered from these references internet survey was conducted. In some cases direct information was obtained via personal communication. Afterwards, hazardous wastes generated as a result of that activity is inspected at 6-digit level. In most cases differences in terminology between different references is experienced because generation points of hazardous wastes listed in EWC and Annex 7 of RCHW within a given process is not always clear. This situation requires a close inspection on production processes.

only one type of production processes among several processes that results in the same product. Whenever possible flow diagrams of production processes for each 6-digit entry are obtained and comparison is made with BREFs and EWC. The type of production processes for which waste generation factors are found should match with the production processes being applied in Turkey. Only if so, the waste generation factors are used for estimation of hazardous wastes. In the next step, waste generation factors of hazardous wastes produced in the previous step are found. In the last step, calculations were made by using waste generation factors and production capacities related to that industry. Throughout the thesis waste entries and entry codes are written in italics.

In Chapters 4 – 17, calculations made for determination of amount of hazardous wastes classified under different entries in EWC and Annex 7 of the RCHW of Turkey are presented. In Chapters 18 and 19 discussion and conclusions are given. In Chapter 20 recommendations for future studies are discussed.

# **CHAPTER 4**

# WASTES RESULTING FROM EXPLORATION, MINING, QUARRYING AND PHYSICAL AND CHEMICAL TREATMENT OF MINERALS

4.1 Objective and Scope

Objective of this chapter is to determine the amount of hazardous wastes generated in Turkey as a result of mining activities. According to EWC and Annex 7 of RCHW of Turkey, these mining activities cover milling and beneficiation of metalliferous and non-metalliferous minerals [3,19].

#### 4.2 Introduction

Mining operations consists of mining itself and beneficiation in which separation of valuable minerals from the rest is carried out [22]. More detailed information about mining processes and the wastes originating from these processes can be found in Appendix B-1. Copper, silver, gold, iron, chromium and zinc are among the metalliferous minerals mined in Turkey.

4.3 Hazardous Wastes Generated as a Result of Exploration, Mining, Quarrying and Physical and Chemical Treatment Of Minerals

Mineralogy of ore as well as mineral processes used; effects the characteristics of tailings. The tailings characteristics determine the tailings behavior [30]. If metal ore contains sulfide in the form of metal sulfides, these constituents of ores can become oxidized to form sulfates, hydrogen ions and dissolved metals [30]. Acid generation is largely the result of oxidation of metallic sulfides. The major metallic sulfide of

concern is iron sulfide (FeS<sub>2</sub>), or pyrite. [31]. Due to the fact that characteristics and amount of tailings generated in mining sites is highly dependent on site and ore characteristics the potential of acid generating tailings production is highly variable from site to site.

Hazardous wastes generated as a result of mining activities are covered under 2-digit entry of 01-Wastes resulting from exploration, mining, quarrying, and physical and chemical treatment of minerals. Under this 2-digit entry, only acid generating tailings (01 03 04) are classified as absolute entry. Other than acid generating tailings, other tailings and wastes containing dangerous substances (01 03 05, 01 03 07 and 01 04 07) are listed as minor entries. Lastly, drilling muds (01 05 05, 01 05 06) are given under 01 as minor entries. Complete list of wastes included in wastes resulting from exploration, mining, quarrying, and physical and chemical treatment of minerals-01 can be found in Appendix A.

4.4 Information Required for Determining Hazardous Wastes Generated as a Result of Exploration, Mining, Quarrying and Physical and Chemical Treatment of Minerals

Information required for determination of hazardous waste generation from mining activities can be listed as follows:

- 1 Wastes from physical and chemical processing of metalliferous minerals (01 03):
  - 1.1 The type of metalliferous minerals mined and processed in Turkey: Major types of metalliferous minerals mined and processed in Turkey include copper, silver, gold, iron, chromium and lead-zinc. For the case of lead-zinc, primary production of only zinc occurs in Turkey. Although lead is mined along with zinc, no primary production for lead exists in Turkey.
  - 1.2 Capacities of establishments in which mining and processing of metalliferous minerals occurs: Capacities of main mining sites are given in Table 4. 1. Moreover, yearly productions of metalliferous minerals are presented in Table 4. 2

Material	Name of Facilities	Location	Capacity (tons/yr)	Total capacity (1000 tons/yr)
	Eti Holding A.Ş.	Aşıköy - Bakibaba	3,000,000	
Copper [24]	Karadeniz Bakır İşletmeleri (KBİ)	Murgul	700,000	5,575
	Demir Export A.Ş.	Espiye	125,000	
	Çayeli Madenleri A.Ş.	Çayeli	800,000	
	Ben-Oner A.Ş.	Ergani	950,000	
Silver [25]	Eti Holding Gümüş A.Ş.	Gümüşköy	1,000,000	1,000
Gold [25]	Eurogold Madencilik A.Ş.	Ovacık	300,000	300
	Public facilities	Various		
Iron [26]	Kardemir and İsdemir	Various		
	Erdemir	Various		
Chromium [27]	Etibank Genel Müdürlüğü (Şarkkromları ve Üçköprü İşletmeleri) Akpaş Maden Pazarlama Bilfer Madencilik A.Ş. Birlik Madencilik A.Ş. Bursa Toros Kromları A.Ş. Dedeman Madencilik ve Tic. A.Ş. Güney Doğu Krom İşletmeleri A.Ş. Hayri Ögelman Madencilik Ltd. Şti Köyceğiz Kromları Ltd. Şti Krom-Demir Maden ve Tic Ltd. Şti Krom Çeltek Ltd. Şti Montan Madencilik A.Ş. Mikro Maden Sanayii A.Ş. Mustafa Surucuoğlu Madencilik Ögel Madencilik A.Ş. Pınar Maden Turizm A.Ş. Rasih ve İhsan Maden Ltd. Şti Türk Maadin A.Ş.			>2,080 in total

Table 4. 1: Production in mining industry

Material	Name of Facilities	Location	Capacity (tons/yr)	Total capacity (1000 tons/yr)
	Adana Madencilik	Kozan	30,000	
	Demir Export	Espiye	120,000	
Lead – Zinc	Ben-Oner A.Ş.	Şebinkarahisar	45,000	
	Çanakkale Madencilik	Merkez Korudere	30,000 30,000	410
[28]	İ. Pazarköylü	İvrindi	24,000	
	Menka A.Ş.	Muradin	36,000	
	Rasih İhsan	Akdağ	60,000	
	Samaş A.Ş.	Aladağ	35,000	
TOTAL				9,365

Table 4. 1 continued

- 1.3 Waste generation factors for acid generating tailings: As mentioned above due to the variation in amount and characteristics of tailings it is difficult to develop waste generation factors for minerals. Unfortunately, no tailings generation data is available for Turkey for different mines and minerals. For this reason, the figures belonging to the USA was utilized. Waste generation factor development for metalliferous minerals is discussed in Section 4.5.
- 2 Wastes from physical and chemical processing of non-metalliferous minerals (01 04):
  - 2.1 The type of metalliferous minerals mined and processed in Turkey
  - 2.2 Capacities of establishments in which mining and processing of metalliferous minerals occurs
  - 2.3 Waste generation factors for tailings containing dangerous substances: As in the case of metalliferous minerals, tailing generation is highly dependent on the mineral and characteristics of site and ore to be mined. In EWC and Annex 7 of RCHW of Turkey, no absolute entries are listed for non-metalliferous minerals. Due to lack of information on waste generation factors and tailings generated as a result of non-metalliferous minerals being minor entries no calculation is made for this entry.

	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999
Copper-[24]*					39	43.4	52.2	64.6	73.9	
Silver-[25]	0.026	0.039	0.077	0.070	0.068	0.053	0.070	0.076	0.086	0.088
Gold										
Iron-[26]*	4,708	4,726	4,825	5,070	5,079	5,510	5,150	4,800	5,142	3,797
Chromium-[27]				767.3	1,270.4	2,080	1,279	1,646.4	1,440	777.3 **
Ferrochromium- [27]				90,030	97,585	94,251	101,450	100,000		
Lead-Zinc-[28]	397	262	225	254	256	562	316			
Zinc-[28]*	143	102	254	252	321	822	812.8	-	-	-

 Table 4. 2: Annual productions of selected metals (1000 tons)

\* Ore production

\*\* Production in the first 9 month of the year 1999

#### **3** Drilling muds and other drilling wastes (01 05):

- 3.1 **Drilling sites where drilling muds are utilized in Turkey**: No data is available regarding the use drilling muds in Turkey.
- 3.2 Type of the drilling muds used: In EWC and Annex 7 of RCHW of Turkey oil containing drilling muds is classified under a different entry. For this reason, type of drilling muds utilized should be known. Unfortunately, no information could be obtained regarding the types of drilling muds used in Turkey.
- 3.3 Waste generation factor for drilling muds/amount of drilling muds used in Turkey: Drilling muds are utilized in a continuous manner to prevent friction throughout the drilling process. As a result, no waste generation factor is available in the literature for drilling muds. This is because of the fact that; depending on the geology of the drilling site and properties of drilling machines etc. each drilling operation requires different amounts of drilling muds. A second approach for determining the amount of drilling muds wasted can be to determine the total amount of drilling muds utilized in Turkey assuming all the drilling muds used are wasted. However, as mentioned above no data is available regarding the use of drilling muds in Turkey. In summary, no calculation could be made for the amount of hazardous waste generation as a result of drilling muds.
- 4.5 Hazardous Waste Generation Factors for the Wastes Resulting from Exploration, Mining, Quarrying and Physical and Chemical Treatment of Minerals

In developing waste generation factors for the mining operations; since there is no data available for Turkey, the figures belonging to the USA was utilized. Based on the data published by US EPA, the amounts of minerals produced and tailings generated in United States are as given in Table 4. 3. Waste generation factors were determined by using the minerals production and tailings generation data given in Table 4. 3. In order to develop waste factors for tailings generated as a result of production of each mineral, the amount of production is divided by the amount of that commodity

Commodity	Material Handled	Waste Rock			Or		Total waste (waste rock + tailings)		
Commonly	(1,000 tons)		%	Tai	ings	Pro	duct	1,000	%
	(1,000 tons)	1,000 tons	material	1,000 tons	% material	1,000 tons	% material	tons	material
Copper	732,831	393,332	53.7	337,733	46.1	1,765	0.2	731,065	99.8
Silver	>2,824	-	-	2,822	99.9	1.8	0.1	2,822	99.9
Gold	540,661	293,128	54	247,533	46	0.329	0.00006	540,661	99.99
Iron	242,029	1067,233	43.9	80,204	33.1	55,593	23	186,437	77
Lead	>6,759	-	-	6,361	94.1	398	5.9	6.361	94.1
Zinc	4,751	-	-	4,227	89	524	11	4,227	89

 Table 4. 3: Amounts of minerals produced and tailings generated in United States [32]

handled. By this way, the amounts of tailings generated for unit amount of mineral handled is found. These findings are summarized in Table 4. 4.

	Tailings generated (tons)				
	Per material handled (ton)	Per product (ton)			
Copper	0.46	191.4			
Silver	0.99	1,567.8			
Gold	0.46	752,380.0			
Iron	0.33	1.4			
Lead	0.94	16.0			
Zinc	0.89	8.0			

Table 4. 4: Waste generation factors for tailings generated in USA

- 4.6 Hazardous Waste Generation from Exploration, Mining, Quarrying and Physical and Chemical Treatment of Minerals in Turkey
  - Hazardous waste generation from physical and chemical processing of metalliferous minerals (01 03): Using the tailings generation factors in terms of both material handled and product given in Table 4. 4, amount of tailings generated can approximately be estimated for the selected minerals in Turkey. Table 4. 5 summarizes the results for this calculation carried out for the period of 1990 to 1999.

It is obvious that the ultimate aim in the present study is to develop a typical tailings generation figure for the mining industry in Turkey. However, it was not possible to estimate the total amount of tailings generated as a result of mining of all the minerals per year since data related to mineral ore production for different minerals do not exists for each year. However, an average tailing generation per year can be estimated as given in Table 4. 6 based on the available data.

Year	1990	1991	1992	1993	1994
Material	Tailings generated (tons)	Tailings generated (tons)	Tailings generated (tons)	Tailings generated (tons)	Tailings generated (tons)
Copper					17,900
Silver	40,800	61,100	120,720	109,750	106,600
Iron	1,553,640	1,559,580	1,592,250	1,673,100	1,676,070
Zinc	127,591	91,166	226,560	224,724	285,965

Table 4. 5: Amounts of tailings generated in Turkey for various metals

Year	1995	1996	1997	1998	1999
Material	Tailings generated (tons)	Tailings generated (tons)	Tailings generated (tons)	Tailings generated (tons)	Tailings generated (tons)
Copper	20,000	24,000	29,700	34,000	
Silver	83,100	109,750	119,150	134,830	137,970
Iron	1,818,300	1,699,500	1,584,000	1,696,860	1,253,010
Zinc	731,933	723,392			

Table 4. 5: continued

 Table 4. 6: Waste generation for 01 03 04
 Output

Mineral	Average tailing generation(1,000 t/yr)
Copper	25
Silver	103
Iron	1,610
Zinc	380
TOTAL	2,118

Findings obtained regarding *wastes resulting from exploration, mining, quarrying, and physical and chemical treatment of minerals-01* is summarized in Table 4. 7.

#### 4.7 Comments

Acid generation capacity of the tailings depends on the mineralogy of mineral in a specific mine site. According to the literature production of base metals (cadmium, copper, lead, nickel, tin and zinc) and precious metals result in higher amounts of acid generating tailings, whereas, production metals like aluminum, chromium, iron and tungsten do not result in acid generating tailings. Thus, although amounts of tailings generated can be estimated, the extent of tailing generation that would fall into the entry of *acid-generating tailings from processing of sulfide ore* (01 03 04) would be site and mineral specific. Therefore, to obtain most accurate results in terms of entry 01 03 04, it necessary to conduct analysis on tailings of mining sites in Turkey.

In Potential Environmental Impacts of Hardrock Mining published by Environmental Protection Agency of United States (USEPA) the amount of ore mined and tailings generated is given for selected minerals. Waste factors developed for the calculation of tailing generation amount are adopted from this document.

Name of the entry			Amount generated (t/yr)		
2-digit	4-digit	6-digit	6-digit	4 digit	2 digit
		Acid generating tailings from processing of sulfide ore (01 03 04)			
	Wastes from physical and chemical processing of	Other tailings containing dangerous substances (01 03 05)	2,118,000	2,118,000	
Wastes resulting from exploration, mining, metalliferous m 03)	metalliferous minerals (01 03)	Other wastes containing dangerous substances from physical and chemical processing of metalliferous minerals (01 03 07)	2,118,00		
quarrying, and physical and chemical treatment of	Wastes from physical and chemical processing of non- metalliferous minerals (01 04)	Wastes containing dangerous substances from physical and chemical processing of non- metalliferous minerals (01 04 07)			2,118,000
	Drilling muds and other drilling wastes (01 05)	Oil containing drilling muds (01 05 05) Drilling muds and other drilling wastes containing dangerous substances (01 05 06)			

Table 4.7: Results obtained for wastes resulting from exploration, mining, quarrying, and physical and chemical treatment of minerals (01)

However, in order to make a good estimation for tailings generated as a result of mining activities in Turkey it is necessary to develop waste factors for Turkish mines because calculations done for Turkey using waste factors adopted from USEPA documents may not represent the situation in Turkey correctly. Another problem associated for this entry is that the exact sulfide content of the ores are not known which may lead to an overestimation when all the tailings generated are categorized as hazardous wastes under entry *01 03 04*.

Wastes from physical and chemical processing of non-metalliferous minerals (01 04) contain a single minor entry which is wastes containing dangerous substances from physical and chemical processing of non-metalliferous substances (01 04 07). The wastes produced in Turkey that fall under the entry of 01 04 07 need to be analyzed to determine whether they are hazardous or not since it is a minor entry.

#### **CHAPTER 5**

## WASTES FROM WOOD PROCESSING

#### 5.1 Objective and Scope

Objective of this chapter is to determine the amount of hazardous wastes generated as a result of wastes from wood processing. According to EWC and Annex 7 of RCHW of Turkey wood processing activities include wood processing and production of panels and furniture, wood preservation and pulp, paper and cardboard production [3, 19]. In this chapter, main emphasis is given to wood preservation which produces higher amounts of hazardous wastes.

#### 5.2 Introduction

Wood preservatives are used to delay wood deterioration and decay caused by wood destroying organisms such as insects, fungi, and marine borers. The deep penetration is usually accomplished by forcing preservative into the wood under pressure main wood preservatives currently in use are pentachlorophenol, creosote, and inorganic arsenical and/or chromate salts [33].

Most commonly used wood preservatives are formulations of pentachlorophenol, creosote, and inorganic arsenical and/or chromate salts [33] although wood preservatives may not be limited to these substances and some other formulations may be used for the preservation of wood. First of the three most commonly used wood preservatives is the pentachlorophenol which as the name implies contain chlorine in its formulation. Creosotes contain mixtures of relatively heavy residual oils obtained from the distillation of tar or crude petroleum. The third most commonly used preservative is the inorganic ones [33]. In Appendix B-2, information about wood preservation processes and types of wood preservatives is given in more detail.

#### 5.3 Hazardous Wastes Generated as a Result of Wood Processing

Hazardous wastes produced as a result of wood processing activities are included in *wastes from wood processing and the production of panels and furniture, pulp and paper and cardboard (03)* in EWC and Annex 7 of RCHW of Turkey [3, 19]. Wood processing and the production of panels and furniture, pulp, paper and cardboard (03) contains two 4-digit entries which are *wastes from wood processing and production of panels and furniture (03 01)* and *wastes from wood processing and production of panels and furniture (03 01)* and *wastes from wood processing and production of panels and furniture (03 01)* and *wastes from wood preservation (03 02)*. 03 01 contains a single minor entry covering sawdust, shavings cuttings, wood, particle board and veneer containing dangerous substances (03 01 04). Whereas, under the 4-digit entry of 03 02, five 6-digit absolute entries exist [3,19]. Among these 6-digit entries except the entry other wood preservative containing dangerous substances (03 02 01), organochlorinated wood preservatives (03 02 02), organometallic wood preservatives (03 02 03), inorganic wood preservatives (03 02 04) are regarded as absolute entries. These entries cover wasted wood preservatives of different types [3,19]. In Appendix A, complete list of wastes listed under 03 can be found.

5.4 Information Required for Determining Hazardous Wastes Generated from Wood Processing

Information required for determination of hazardous waste generation from organic chemical processes can be listed as follows:

 Capacity information related to wood preservation industry: According to Union of Chambers and Commodity of Exchanges (TOBB) Industry Database<sup>1</sup> 1,545,656 m<sup>3</sup> of wood is processed yearly for preservation [34] with a total of 34 facilities.

<sup>&</sup>lt;sup>1</sup> TOBB Industry Database contains 66,000 entries throughout Turkey.

- **2** Types and amounts of wood preservatives used: In EWC and Annex 7 of RCHW of Turkey, wastes generated as a result of utilization of different types of wood preservatives are classified under different entries. Unfortunately, no data regarding types and utilization amount of preservatives is available.
- **3** Waste generation factors for types of wood preservatives listed in EWC and Annex 7 of RCHW: Another important information required for the determination of hazardous wastes generated is waste generation factors developed for different types of wood preservatives. Waste generation factors gathered from the literature are given in Section 5.5.
- 5.5 Hazardous Waste Generation Factors for Wood Preservation Wastes

In general 64 to 1200 liters of wastewater per cubic meter of wood may be generated. The average process wastewater generation rate is 174 L/m<sup>3</sup> of treated wood for the 14 plants supplying both production and wastewater generation information in response to the RCRA 3007 Survey [33].

In Best Demonstrated Available Technology (BDAT) Background Document for Wood Preserving Wastes, average free drippage is assumed to be 1 L/m<sup>3</sup> of treated wood [33]. In terms of drip pad sludges average generation factor is estimated to be  $0.0462 \text{ L/m}^3$  of treated wood. A summary of waste generation factors that are given in Table 5. 1.

Waste type	Process/ type of preservative used	Waste generation factor
Wastewater	General	$174 \text{ L/m}^3$ of treated wood
Free drippage	General	1 L/m <sup>3</sup> of treated wood
Process sludge or residual	Creosote	$0.542 \text{ L/m}^3$ of treated wood
Process sludge or residual	Pentachlorophenol	$0.845 \text{ L/m}^3$ of treated wood
Process sludge or residual	Inorganic	$0.051 \text{ L/m}^3$ of treated wood
Drip pad sludges	General	0.0462 L/m <sup>3</sup> of treated wood

Table 5. 1: Waste generation factors for wood preservation processes

#### 5.6 Hazardous Waste Generation from Wood Preservation in Turkey

• Hazardous waste generation from wood preservation (03 02): As it is mentioned in Section 5.4, it does not seem possible to determine the utilization of each type of preservative in Turkey. Residual generation factors from application of different types of preservatives are known and these residuals fall into different entries in EWC and Annex 7 of the RCHW. Since the extent of use of these materials is not known separately, calculations can be done so that maximum amount of residuals is found by assigning total wood preservation data to each wood preservative. Alternatively, an average value for residual generation can be found by assigning <sup>1</sup>/<sub>3</sub> of total amount of wood treated to each type of widely used wood preservative. It is concluded that later approach would give a more practical result in a sense that by this way a single estimation will be obtained instead of three different estimates.

By using waste generation factors tabulated in Table 5. 1 and amount of wood treated for preservation given in Section 5.4, hazardous waste generation from wood preservation processes are calculated. Results are given in Table 5. 2 along with the number of entry these wastes fall into.

Waste type	Entry	Waste generation (m <sup>3</sup> /yr)
	03 02 01	
Wastewater	03 02 02	270,000
wastewater	03 02 03	270,000
	$03\ 02\ 04^{*}$	
	03 02 01	
Free drippage	03 02 02	1,545
Thee drippage	03 02 03	1,545
	$03\ 02\ 04^{*}$	
Creosote residual or sludge	03 02 01	840
Pentachlorophenol residual or sludge	03 02 02	1,300
Inorganic residual or sludge	03 02 04	80
	03 02 01	
Average for process residuals	03 02 02	740
	03 02 04	
	03 02 01	
Drip pad sludges	03 02 02	72
Drip pad sludges	03 02 03	12
	03 02 04 *	
TOTAL		272,000

Table 5. 2: Amount of hazardous wastes generated from wood preservation in Turkey

Findings regarding wastes from wood processing and the production of panels and furniture, pulp, paper and cardboard (03) are presented in Table 5. 3.

#### 5.7 Comments

Attention was given to wood preservation wastes that contain absolute entries since data related to wood processing industry is not adequate. This is due to fact that wood processing industry comprises largely numerous small scale facilities. Gathering capacity information about these small scale facilities poses a problem.

The only group of absolute hazardous wastes contained in *wastes from wood* processing and the production of panels and furniture, pulp, paper and cardboard (03) are wastes from wood preservation (03 02). Capacity related to wood preservation industry was found whereas it was not possible to determine the amount of different types of wood preservatives used. Since the extent of use of these materials are not known separately, an average value for residual generation can be found by assigning  $\frac{1}{3}$  of total amount of wood treated to each type of widely used wood preservative.

Name of the entry			Amount generated (t/yr)		/yr)
2-digit	4-digit	6-digit	6-digit	4 digit	2 digit
Wastes from wood processing	Wastes from wood processing and the production of panels and furniture (03 01)	Sawdust, shavings, cuttings, wood, particle board and veneer containing dangerous substances (03 01 04)			
and the production of		Non-halogenated organic wood preservatives (03 02 01)		680,000 *	680,000
panels and	Ward on farming 1	Organochlorinated wood preservatives(03 02 02)			
furniture, pulp, paper and	Wastes from wood preservation (03 02)	Organometallic wood preservatives (03 02 03)			
	preservation (05 02)	Inorganic wood preservatives (03 02 04)			
cardboard (03)		<i>Other wood preservatives containing dangerous</i> <i>substances</i> (03 02 05)			

Table 5. 3: Results obtained for wastes from wood processing and the production of panels and furniture, pulp, paper and cardboard (03)

 $<sup>^{\</sup>ast}$  Assuming average density of wood preservatives as 2.5 t/m  $^{3}$ 

## **CHAPTER 6**

# WASTES FROM PETROLEUM REFINING NATURAL GAS PURIFICATION AND PYROLYTIC TREATMENT OF COAL

#### 6.1 Objective and Scope

Objective of this chapter is to determine the amount of hazardous wastes generated from petroleum refining and pyrolytic treatment of coal. According to EWC and Annex 7 of RCHW of Turkey, related industries are petroleum refining, pyrolytic treatment of coal and natural gas purification and transportation.

## 6.2 Introduction

Petroleum refining is the physical, thermal and chemical separation of crude oil into its major distillation fractions, which are then further, processed through a series of separation and conversion steps into finished petroleum products. Appendix B-3 summarizes the petroleum refining processes. Currently, there are four refineries in Turkey all of which are owned by TÜPRAŞ.

6.3 Hazardous Wastes Generated as a Result of Petroleum Refining and Pyrolytic Treatment of Coal

According to EWC and Annex 7 of the RCHW, *wastes from petroleum refining natural gas purification and pyrolytic treatment of coal (05)* contains three 4-digit entries; namely *wastes from petroleum refining (05 01)*, *wastes from pyrolytic treatment of coal (05 06)* and *wastes from natural gas purification and transportation (05 07)*. Under *wastes from petroleum refining (05 01)* sludges, tars, oil containing acids and spent filter clays are listed as hazardous wastes.

Under *wastes from natural gas purification and transportation* only one entry that is wastes containing mercury is listed as a minor entry [3, 19]. Complete list of wastes listed under wastes from petroleum refining and pyrolytic treatment of coal are given in Appendix A.

6.4 Information Required for Determining Hazardous Wastes Generated from Petroleum Refining, Natural Gas Purification and Pyrolytic Treatment of Coal

### 1 Wastes from petroleum refining (05 01):

1.1 Total capacities of refineries in terms of crude oil: In the year 2003, 26.934 million tons of crude oil was processed of which 24 million was processed in TÜPRAŞ refineries and 2.934 million tons were processed in ATAŞ refinery [36]. In Table 6. 1, capacities of TÜPRAŞ refineries and amount of crude oil processed in the year 2003 are given. ATAŞ Refinery is not included since recently it is closed.

Refineries	Capacity (million tons)	Crude oil processed (million tons)	Capacity usage (%)
İzmit	11.5	9.7	83.9
İzmir	10.0	9.7	97.0
Kırıkkale	5.0	3.7	73.2
Batman	1.1	0.9	83.9
TOTAL	27.6	23.9	86.7

Table 6. 1: Capacities of refineries and amount of crude oil processed in 2003 [36]

1.2 Determination processes applied in each refinery and capacities of these processes: In relation with the properties of crude oil processed and variety of desired end-products, different processes are applied in each refinery around the world. This situation is also valid for Turkish refineries. Moreover, refinery operations and processes are not independent from each other. This is due to the fact that undesired process residuals from previous processes may be used to form desired end-products or a fraction in subsequent processes and operations are further processed to form various other end-products. One last aspect of refineries worth mentioning is that in addition to feed and product variety, facility management including material recovery from

undesired fractions such as tank bottom residuals or desalter residuals and maintenance practices will differ from refinery to refinery. All these facts necessitate a good understanding on the types of processes applied in each refinery in Turkey. Types of processes applied in refineries are identified using process diagrams and list of these processes are given in Table 6. 2 [103].

1.3 **Capacities of processes applied in refineries**: Capacities of processes applied in each refinery are given in Table 6.2.

Refinery	Process Plant	Capacity	Unit				
	Crude oil and intermediary product processing units						
	Crude oil units	36,000	m <sup>3</sup> /d				
	Vacuum units	14,200	m <sup>3</sup> /d				
	FCC (conversion) unit	2,200	m <sup>3</sup> /d				
	Hydrocraker unit	3,656	m <sup>3</sup> /d				
	Reformer (Octane enhancement) unit	3,225	m <sup>3</sup> /d				
TÜPRAŞ	Isomerization unit	2,628	m <sup>3</sup> /d				
I UP KAŞ İzmit	Desulfurizer units	6,900	m <sup>3</sup> /d				
Refinery	Sulfur recovery units	137	tons/d				
Кејшегу	Storage capacities for crude oil and product	ts					
	Crude oil storage	915,000	m <sup>3</sup> (gross)				
	Product and intermediate product storage	877,000	m <sup>3</sup> (gross)				
	Wastewater treatment units						
	Industrial wastewater treatment unit	1,000	m <sup>3</sup> /hr				
	Ballast water treatment unit	750	m <sup>3</sup> /hr				
	Domestic wastewater treatment unit	550	m <sup>3</sup> /d				
	Crude oil and intermediary product processing units						
	Crude oil units	36,000	m <sup>3</sup> /d				
	Vacuum units	12,672	m <sup>3</sup> /d				
	FCC (conversion) unit	2,208	$m^{3}/d$				
	Hydrocraker unit	2,616	m <sup>3</sup> /d				
	Reformer (Octane enhancement) unit	4,668	$m^3/d$				
	Isomerization unit	1,908	m <sup>3</sup> /d				
TÜPRAŞ	Desulfurizer units	2,880	m <sup>3</sup> /d				
İzmir	Visbreaking units	3,100	m <sup>3</sup> /d				
Refinery	Sulfur recovery units	113	tons/d				
	Storage capacities for crude oil and product	<u>ts</u>					
	Crude oil storage	590,000	m <sup>3</sup> (gross)				
	Product and intermediate product storage	1,045,000	m <sup>3</sup> (gross)				
	Wastewater treatment units	•					
	Industrial wastewater treatment unit	2 * 600	m <sup>3</sup> /hr				
	Ballast water treatment unit	2 * 260	$m^3/d$				
	Domestic wastewater treatment unit	150	m <sup>3</sup> /hr				

 Table 6. 2: Capacities of process plants [36]

Refinery	Process Plant	Capacity	Unit				
-	Crude oil and intermediary product processing units						
	Crude oil units	18,000	m <sup>3</sup> /d				
	Vacuum units	4,800	$m^{3}/d$				
	Hydrocraker unit	2,300	m <sup>3</sup> /d				
	Reformer (Octane enhancement) unit	3,200	$m^3/d$				
TÜPRAŞ	Isomerization unit	1,435	m <sup>3</sup> /d				
Kırıkkale	Desulfurizer units	2,700	m <sup>3</sup> /d				
Refinery	Sulfur recovery units	83	tons/d				
	Storage capacities for crude oil and products						
	Crude oil storage	471,000	m <sup>3</sup> (gross)				
	Product and intermediate product storage	m <sup>3</sup> (gross)					
	Wastewater treatment units						
	Wastewater treatment unit	630	m <sup>3</sup> /hr				
	Crude oil and intermediary product processing units						
	Crude oil units	3,500	$m^3/d$				
	Vacuum units	340	m <sup>3</sup> /d				
TÜPRAŞ	Reformer (Octane enhancement) unit	215	$m^3/d$				
Batman	Storage capacities for crude oil and products						
Refinery	Crude oil storage	32,000	m <sup>3</sup> (gross)				
	Product and intermediate product storage	123,000	m <sup>3</sup> (gross)				
	Wastewater treatment units						
	Wastewater treatment unit	290	m <sup>3</sup> /hr				

Table 6. 2 continued [36]

1.4 **Waste generation factors for petroleum refining**: Since a wide variety of processes are applied in refineries waste generation factors should be identified. Waste generation factors are discussed in more detail in Section 6.5.

#### 2 Wastes from pyrolytic treatment of coal (05 02):

- 2.1 **Capacities of facilities applying pyrolytic treatment of coal**: No capacity information could be reached regarding pyrolytic treatment of coal in Turkey.
- 2.2 **Waste generation factors for pyrolytic treatment of coal**: No waste generation factor could be found for pyrolytic treatment of coal. Since neither capacities nor waste generation factors could be found no further calculation could be made.

#### **3** Wastes from natural gas purification and transportation:

- 3.1 **Capacities of gas purification and transport facilities**: No capacity information could be found for facilities of natural gas purification and transportation.
- 3.2 Waste generation factors for natural gas purification and transportation: No waste generation factor could be reached regarding natural gas purification and transportation. Since neither capacities nor waste generation factors could be found no further calculation could be made.
- 6.5 Hazardous Waste Generation Factors for Petroleum Refining Wastes

Overall quantity of wastewater originating from each refinery depends on the processes used in the refinery. Therefore, it is necessary to acquire information about types of processes applied in refineries. When wastewater generation from each process is known overall wastewater generation can be found [38].

In order to determine the waste factor for tank bottom sludge, total amount of tank bottom sludge reported by 125 refineries in year 1992 as 9,107 Mton was used. The amount of crude oil processed in United States is also known as 749 million m<sup>3</sup>/yr [40, 41, 42]. From these two values, waste factor is calculated as 0.098 ton/m<sup>3</sup> of crude oil stored per year.

Waste generation factors for each refining process should be examined in order to determine the total hazardous waste generation. For this purpose Table 6. 3 is prepared containing waste generation factors and information about constituents of wastes where available [38]. In this table, information related to two major groups of wastes; wastewaters and sludges is given. Here, sludge contains some other groups of wastes such as spent catalysts.

		Wastewater		Sludg	e
Name of the process	Properties of process Wastewater			Properties of sludge	Constituents
Alkylation		Hydrocarbons	Acid		
Sulfuric acid	Low pH, contains,		Sulfuric acid		
Hydrofluoric	H <sub>2</sub> S and spent acid		Effluents from HF scrubber are 2 – 8 m <sup>3</sup> /h		7 – 70 kg sludge per kg used HF
Base oil production	1				
Deasphalting		Solvent recovery stage results in solvent- contaminated water, oil components			
Aromatic extraction	2 – 4 m <sup>3</sup> /ton of product				
Solvent dewaxing		Solvent-co	ontaminated water		
Hydrofinishing	Leakages from equipment				
Bitumen production	5 m <sup>3</sup> /ton of feed	Contains H <sub>2</sub> S, oil aromatics, PAHs, sulfuric acid, odorous oxidation products			Slop oil emulsions of light oil, water and particulates
Catalytic cracking	Steam: flow 20 – 40 m <sup>3</sup> /h, caustic washing of hydrocarbons: Flow 128 m <sup>3</sup> /h			Replacement of old catalyst: 50 t/4 yr, tank sludge slurry: depends on slurry filtration systems	

# Table 6. 3: Wastes originating from petroleum refining processes [38]

	Waste	water	Slu	ıdge
Name of the process	Properties of process wastewater	Constituent	Properties of sludge	Constituents
Catalytic reforming	1 - 3 L/ ton of feedstock	High-levels oils, suspended solids	Spent catalyst: 20 – 25 t/yr for a 5 Mton/yr refinery	
Coking processes	25 L/ ton of feedstock	H <sub>2</sub> S <sub>1</sub> coke fines with high metal contents, high pH, hydrocarbons, sulfur compounds, cyanides, and phenols.	Hot oil blow-down sludges	
Cooling systems	Water blow-down discharge: 26,000 m <sup>3</sup> /hr (once through), 156 m <sup>3</sup> /hr (cooling towers)	Hydrocarbons, chemical conditioning		
Desalting	30 – 100 L/ t feedstock desalted), high temperature salt water waste stream	High oil/oil emulsions, dissolved hydrocarbons, Phenols, Benzene, Ammonia, nitrogen compounds, sulfides- H <sub>2</sub> S	Quantities depend on solid content of crude, separation efficiency and desluding practice 60 - 1,500  t/yr	Iron lust, clay, sand water $(5 - 10\%)$ , emulsified oil and wax (20 - 50%  w/w), metals
Energy system	Originates from boiler feed water, boiler blow- down:		Depends on furnace design and liquid fuel quality, 0 – 10 tons/yr,	
Etherification	$1 - 2 \text{ m}^3/\text{t}$	Methanol, ethanol, ethers, formic acid, acetic acid		

# Table 6. 3 continued [38]

	Wastewater		Sludge		
Name of the process	Properties of process Wastewater	Constituent	Properties of sludge	Constituents	
Gas separation processes		Hydrocarbons, H <sub>2</sub> S, NH <sub>3</sub> and amines			
Hydrogen consuming p	rocesses				
Hydrotreatment	30 – 55 L/t	H <sub>2</sub> S, NH <sub>3</sub> , high pH, phenols, hydrocarbons, suspended solids			
Hydrocracking	50 – 110 L/t	Suspended solids,			
Hydrogen production					
Isomerization		Chloride salts, caustic wash			
Natural gas plants		Organic contaminant	250 – 400 tons/yr	12 kg Hg/1,000 kg sludge	
Polymerisation	Low pH	Hydrocarbons from sour water purge from washtower, condenser drains and spillages particulate matter, caustic, wash and sour water with amines and merceptans, H <sub>2</sub> S, NH <sub>3</sub>			
Primary distillation units	$0.08 - 0.75 \text{ m}^3$ /ton of crude oil	,	Sludges from cleaning- out of the columns, 6.3 – 20 t/day for a crude unit of 8,7 Mt/yr		

# Table 6. 3 continued [38]

	Wastewater		Sludge	
Name of the process	Properties of process Wastewater	Constituent	Properties of sludge	Constituents
Product treatments			Waste oily disulphide stream, spent caustic: 0.05 – 1.0 kg/ ton feed	Contains phenols and sulfides, organic compounds: >50 g/L
Storage and handling of refinery materials	Liquid tank bottoms	<5 g/L oil content	Storage tank bottom sludge 0.098 ton/m <sup>3</sup> crude oil	
Visbreaking	56 L/ton of feedstock High pH		Generated from cleaning and turnaround of the process 20 – 25 tons/yr for 5 Mton/yr refinery	
Emissions from wastewater treatment techniques		Releases from effluent depending on treatment efficiency refinery processes	2400 tons/yr for a throughput of 600 m <sup>3</sup> /h, air flotation: 600 tons/yr for 600 m <sup>3</sup> /yr flowrate	API sludge (phenols, metals, up to %10 oils), chemical precipitation sludge, DAF floats (up to 30% oil), biological sludge (metals, <5% oil, suspended solids)

# Table 6. 3 continued [38]

Note that not all of the processes generate wastewater or sludge as a waste. Also note that not all the wastes given in Table 6. 3 are hazardous.

Among possible processes applied in refineries highest wastewater generation belongs to cooling systems which results in water blow-down discharge of 26,000 m<sup>3</sup>/hr and 156 m<sup>3</sup>/hr from cooling towers. The range of wastewater generation in refineries is  $1*10^{-3} - 5$  m<sup>3</sup>/t of feedstock. In terms of sludge, given that all the crude oil coming to a refinery is cleaned from its impurities followed by a primary distillation unit (atmospheric or vacuum distillation) and high amounts of crude oils is stored before being processed, highest amounts of sludge generation occurs in primary distillation, bitumen production, catalytic reforming, coking processes, desalting, hydrotreatment, primary distillation units, product treatments, storage and handling of refinery materials and wastewater treatment processes result in production of hazardous wastes [38].

#### 6.6 Hazardous Wastes Generation from Petroleum Refining Industry in Turkey

• Hazardous wastes generated as a result of petroleum refining (05 01): Attention was given to petroleum refining processes in terms of entries containing absolute entries since no adequate data could be found on pyrolytic treatment of coal.

Based on capacity information for refineries in Turkey given in Table 6. 2 and waste factors given in summarized in Table 6. 3, an estimate hazardous waste generation in refineries in Turkey is obtained. The amount of wastes generated from petroleum refining is given in Table 6. 4 for each unit. Note that although not specified, all the crude oil entering refineries is being cleared from its impurities before being further processed therefore, capacity of desalting is equal to the amount of crude oil entering the refinery. For primary distillation units, BREF Document on Mineral Oil and Gas Refineries a single waste factor is specified. Thus, it is assumed that for both atmospheric and vacuum distillation this factor applies. As in the case of Table 6. 3, hazardous wastes are given along with non-hazardous wastes in Table 6. 4. Whereas, hazardous waste production from each refinery per year is given Table 6. 5.

Refinery	Process unit	Process unit Capacity		Waste production		ous waste luction
			Wastewater (m <sup>3</sup> /yr)	Sludge (t/yr)	Wastewater	Sludge (t/yr)
	Desalting	$36,000 \text{ m}^3/\text{d}$	900 - 3000 *	60 - 1,500		60 - 1,500
	Crude oil units	$36,000 \text{ m}^3/\text{d}$	3,340 - 31,300 *	9.5 – 30.2 t/d		3,500 - 11,000
	Vacuum units	$14,200 \text{ m}^3/\text{d}$	5,540 - 51,500	9.5 – 50.2 tru		5,500 - 11,000
	FCC (conversion) unit	$2,200 \text{ m}^3/\text{d}$		50 t/4 yr **		
	Hydrocraker unit	$3,656 \text{ m}^3/\text{d}$	165 – 360 ***			
ĉ	Reformer (Octane enhancement) unit	3,225 m <sup>3</sup> /d	2.5 - 7.6 ****	52.5 - 65.7 **		52.5 - 65.7 **
ine	Isomerization unit	$2,628 \text{ m}^3/\text{d}$				
TÜPRAŞ İzmit Refinery	Desulfurizer units	6,900 m <sup>3</sup> /d		36 – 718 (LPG) + 212 – 4,356 (Diesel and kerosene) t/d □		
RA	Sulfur recovery units	137 ton/d				
ÜP	Crude oil storage	915,000 m <sup>3</sup>		90,000		90,000
П	Product and intermediate product storage	877,000 m <sup>3</sup>				
	Industrial wastewater treatment unit	1,000 m <sup>3</sup> /hr		4,000 t		4,000
	Ballast water treatment unit	750 m <sup>3</sup> /hr				
	Domestic wastewater treatment unit	550 m <sup>3</sup> /d				

Table 6. 4: Waste production from refineries

Refinery	Process unit	Conseity	Waste pr	oduction	Hazardous w	aste production
Kennery	Process unit	Capacity	Wastewater (m <sup>3</sup> /d)	Sludge (t/yr)	Wastewater	Sludge (t/yr)
	Desalting	$36,000 \text{ m}^3/\text{d}$	900 - 3000 *	60 - 1,500		60 - 1,500
	Crude oil units	$36,000 \text{ m}^3/\text{d}$	3,235 - 30,337	9.5 – 30.2 t/d		3,500 - 11,000
	Vacuum units	$12,672 \text{ m}^3/\text{d}$	5,255 = 50,557			5,500 - 11,000
	FCC (conversion) unit	$2,208 \text{ m}^{3}/\text{d}$		50 t/4 yr **		
	Hydrocraker unit	$2,616 \text{ m}^3/\text{d}$	118 - 260 ***			
	Reformer (Octane enhancement) unit	4,668 m <sup>3</sup> /d	3.5 – 11 ****	52.5 - 65.7 **		52.5 - 65.7 **
ery	Isomerization unit	$1,908 \text{ m}^{3}/\text{d}$				
TÜPRAŞ İzmir Refinery	Desulfurizer units	2,880 m <sup>3</sup> /d		43 - 859 (LPG) + 62 - 1 268.6 (Gas oil and kerosene)t/d <sup></sup>		
zm	Visbreaking units	$3,100 \text{ m}^{3}/\text{d}$		,		
Ŝ	Lube oil units					
RA	Sulfur recovery units	113 tons/d				
ÜP	Crude oil storage	590,000 m <sup>3</sup>		57,820		57,820
T	Product and intermediate product storage	1,045,000 m <sup>3</sup>				
	Industrial wastewater treatment unit	2 * 600 m <sup>3</sup> /hr		4,800 r		4,800 t
	Ballast water treatment unit	$2 * 260 \text{ m}^3/\text{d}$				
	Domestic wastewater treatment unit	150 m <sup>3</sup> /hr				

Table 6. 4 continued
Refinery	Process unit	Capacity	Waste production		Hazardous waste production	
Kenner y	1 Tocess unit	Capacity	Wastewater (m <sup>3</sup> /d)	Sludge (t/yr)	Wastewater	Sludge (t/yr)
	Desalting unit	$18,000 \text{ m}^3/\text{d}$	$450 - 1,500^{*}$	60 - 1,500		60 - 1,500
	Crude oil units	$18,000 \text{ m}^3/\text{d}$	1515 – 14,200 *	4.75 – 15.10 t/d		1,740 - 5,500
	Vacuum units	$4,800 \text{ m}^3/\text{d}$		4.75 – 15.10 vu		1,740 - 3,500
	Hydrocraker unit	$2,300 \text{ m}^3/\text{d}$	103.5 – 207 ***			
	Reformer (Octane enhancement) unit	3,200 m <sup>3</sup> /d	2.4 - 7.4 ****	22 - 27.3 **		22-27.3 **
	Isomerization unit	$1,435 \text{ m}^{3}/\text{d}$				
efinery	Desulfurizer units	2,700 m <sup>3</sup> /d		15.5 - 308.5 (LPG) + 85 - 1747.5 (Diesel and kerosene) t/d <sup></sup>		
ale R	Sulfur recovery units	83 tons/d				
ukk	Crude oil storage	$471,000 \text{ m}^3$		38,350		38,350
TÜPRAŞ Kırıkkale Refinery	Product and intermediate product storage	643,000 m <sup>3</sup>				
TÜF	Wastewater treatment unit	630 m <sup>3</sup> /hr		2,520		2,520

Table 6. 4 continued

Refinery	Process unit	Capacity	Waste prod	uction	Hazardous w	aste production
Kernier y	1 TOCESS unit	Capacity	Wastewater (m <sup>3</sup> /d)	Sludge (t/yr)	Wastewater	Sludge (t/yr)
	Desalting unit	$3,500 \text{ m}^3/\text{d}$	87 - 290	60 - 1,500		60 - 1,500
<i>S</i> ry	Crude oil units	$3,500 \text{ m}^3/\text{d}$	255 - 2,400*	5 – 6.4 t/d		1825 - 2340
fine	Vacuum units	$340 \text{ m}^{3}/\text{d}$	255 - 2,400	3 – 0.4 <i>U</i> u		1823 - 2340
ın Refinery	Reformer (Octane enhancement) unit	215 m <sup>3</sup> /d	0.16 - 0.5 ****	4.2 - 5.3 **		4.2 - 5.3
<i>imc</i>	Crude oil storage	$32,000 \text{ m}^3$		3,140		3,140
TÜPRAŞ Batman	Product and intermediate product storage	123,000 m <sup>3</sup>				
TÜP	Wastewater treatment unit	290 m <sup>3</sup> /hr		1,160		1,160

Table 6. 4 continued

\*Density of crude oil is assumed to be 831 kg/m<sup>3</sup> based on an average value found for different compositions [42]. \*\*\* Spent catalysts \*\*\*\* Density of heavy vacuum gas oil, which is the feedstock for hydrocracker unit, is taken as 900 kg/m<sup>3</sup> [43] \*\*\*\* Density of heavy naphta, which is the feedstock for reformer unit, is taken as 760 kg/m<sup>3</sup> [44]

Density of LGP is taken as 537 kg/m<sup>3</sup> [45], kerosene as 817.15 kg7m<sup>3</sup> [45], diesel as 827 kg/m<sup>3</sup> [47]
 Density of gas oil is taken as 890 kg/m<sup>3</sup> [42]
 Density of naphtha is taken as 665 kg/m<sup>3</sup> [42]

Refinery	Process unit	Sludge produced (t/yr)
	Desalting	60 - 1,500
	Crude oil units	
	Vacuum units	3,500 - 11,000
iry	FCC (conversion) unit	
ine	Hydrocraker unit	
TÜPRAŞ İzmit Refinery	Reformer (Octane enhancement) unit	52.5 – 65.7 t/yr
it F	Isomerization unit	
Zm	Desulfurizer units	
S I.	Sulfur recovery units	
SA	Crude oil storage	90,000
Idí	Product and intermediate product storage	
ΤĊ	Industrial wastewater treatment unit	4,000
	Ballast water treatment unit	
	Domestic wastewater treatment unit	
	TOTAL	97,600 - 106,565
	Desalting	60 - 1,500
	Crude oil units	
	Vacuum units	3,500 - 11,000
	FCC (conversion) unit	
iry	Hydrocraker unit	
ine	Reformer (Octane enhancement) unit	52.5 - 65.7
Ref	Isomerization unit	
TÜPRAŞ İzmir Refinery	Desulfurizer units	
zm	Visbreaking units	
Ž.	Lube oil units	
SA	Sulfur recovery units	
Idí	Crude oil storage	57,820
ΤÜ	Product and intermediate product storage	
	Industrial wastewater treatment unit	4,800
	Ballast water treatment unit	
	Domestic wastewater treatment unit	
	TOTAL	66,960 - 75,200
	Desalting unit	60 - 1,500
ery	Crude oil units	1 740 5 500
line	Vacuum units	1,740 - 5,500
Re	Hydrocraker unit	
ale	Reformer (Octane enhancement) unit	22 - 27.3
kke	Isomerization unit	
	Desulfurizer units	
TÜPRAŞ Kırıkkale Refinery	Sulfur recovery units	
AŞ	Crude oil storage	38,350
PR	Product and intermediate product storage	
ΓÜ	Wastewater treatment unit	2,520
	TOTAL	42,700 - 47,900
-	·	·

Table 6. 5: Hazardous waste production per year from petroleum refiners in Turkey

Table 6. 5 co	ntinued
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Refinery	Process unit	Sludge produced (t/yr)
	Desalting unit	60 - 1,500
u	Crude oil units	1825 - 2340
j m	Vacuum units	1823 - 2340
TÜPRAŞ Batman Refinery	Reformer (Octane enhancement) unit	4.2 - 5.3
[S]	Crude oil storage	3,150
RARe	Product and intermediate product	
E.	storage	
E	Wastewater treatment unit	1,160
	TOTAL	6,200 - 8,150
Turkey	TOTAL	213,500 - 237,800

Categories of hazardous wastes as they are listed in EWC and Annex 7 of the RCHW are tabulated in Table 6. 6.

Entry	Type of entry	Hazardous waste	Quantity generated per year (t/yr)
05 01 02	Absolute entry	Desalter sludge	240 - 6,000
05 01 03	Absolute entry	Tank bottom sludges (from distillation and storage)	200,000 - 219,000
05 01 09	Minor entry	Sludge from wastewater treatment plant	12,500
16 08 07	Minor entry	Spent catalysts	131.2 – 164
TOTAL			213,500 - 237,800

 Table 6. 6: Type of hazardous wastes generated from petroleum refining

Information gathered regarding hazardous wastes generated under *wastes from petroleum refining, natural gas purification and pyrolytic treatment of coal- 05* are summarized in Table 6. 7.

# 6.7 Comments

Oil spills, oily sludges from maintenance operations of the plant or equipment, wastes from cleaning of fuels with bases are specific to plant meaning that different amounts of these wastes are produced in different refineries depending on the refinery practices therefore; it was not possible to develop a waste factor for these items specified in EWC.

Name of the entry		Amount gene	erated (t/yr)		
2-digit	4-digit	6-digit	6-digit	4 digit	2 digit
		Desalter sludges (05 01 02)	240 - 6,000 200,000 -		
		Tank bottom sludges (05 01 03)			
		Acid alkyl sludges (05 01 04)			
		<i>Oil spills (05 01 05)</i>			
		<i>Oily sludges from maintenance operations</i> <i>of the plant or equipment (05 01 06)</i>			
Wastes from	Wastes from petroleum refining (05 01)	Acid tars (05 01 07)		213,500 -	
petroleum		Other tars (05 01 08)		237,800	
refining, natural gas purification and pyrolytic		Sludges from on-site effluent treatment containing dangerous substances (05 01 09)	12,500		213,500 - 237,800
treatment of coal (05)		Wastes from cleaning of fuels with bases (05 01 11)			
		Oil containing acids (05 01 12)			
		Spent filter clays (05 01 15)			
	Wastes from pyrolytic	Acid tars (05 06 01)			
	treatment of coal (05 06)	Other tars (05 06 03)			
	Wastes from natural gas purification and transportation (05 07)	Wastes containing mercury (05 07 01)			

 Table 6. 7: Results obtained for wastes from petroleum refining, natural gas purification and pyrolytic treatment of coal (05)

# **CHAPTER 7**

# WASTES FROM INORGANIC CHEMICAL PROCESSES

#### 7.1 Objective and Scope

Objective of this chapter is to determine the amount of hazardous wastes generated as a result of inorganic chemical processes. According to EWC and Annex 7 of RCHW of Turkey, inorganic chemical processes include manufacture, formulation, supply and use (mfsu) of acids, mfsu of bases, mfsu of salts and their solutions and metallic oxides, mfsu of sulfur chemicals, sulfur chemical processes and desulphurization processes, mfsu of halogens and halogen chemical processes, mfsu of silicon and silicon derivatives, mfsu of phosphorus chemicals and phosphorus chemical processes, mfsu of nitrogen chemicals, nitrogen chemical processes and fertilizer manufacture and manufacture of inorganic pigments and opacificiers.

# 7.2 Introduction

Inorganic chemical processes include a wide variety of processes in which inorganic chemicals are either manufactured, formulated, supplied or used. Among these inorganic chemicals acids, bases, halogens, salts, sulfur, phosphorus, nitrogen chemicals and pigments and opacifiers are found. Especially acids and bases are used in many chemical processes and they may be generated as co-products throughout processes. It is difficult to list all the processes in which inorganic chemical processes used and produced. Explosives manufacture can be given as an example to the processes in which acids are used in high amounts. Another example of inorganic chemical processes is chlorine manufacture. In chlorine manufacture, besides the halogen sodium hydroxide, that is a base is produced.

### 7.3 Hazardous Wastes Generated as a Result of Inorganic Chemical Processes

Wastes from inorganic chemical processes (06) given in EWC and Annex 7 of RCHW include wastes resulting from mfsu of above mentioned inorganic chemicals [3, 19]. In EWC and Annex 7 of RCHW of Turkey, wastes containing all types of acids are classified as absolute hazardous wastes (06 01). This also the case for wastes containing all types of bases (06 02). These wastes are also classified as absolute entries. Another 4-digit entry containing absolute hazardous wastes are *wastes from mfsu of halogens* (06 07) which contain activated carbon from chlorine production(06 07 02) and solutions and acids, for example contact acid (06 07 04) as absolute entries.

Besides wastes from mfsu of acids (06 01), wastes from mfsu bases (06 02) and mfsu of halogens and halogen chemicals (06 07) which contains absolute entries, under wastes from inorganic chemical processes (06), wastes from the mfsu of salts and their solutions and metallic oxides (06 03), metal-containing wastes (06 04), sludges from on-site effluent treatment (06 05), wastes from the mfsu of sulfur chemicals, sulfur chemical processes and desulphurization processes (06 06), wastes from mfsu of silicon and silicon derivatives (06 08), wastes from the mfsu of phosphorus chemicals and phosphorus chemical processes (06 09), wastes from the mfsu of nitrogen chemicals, nitrogen chemical processes and fertilizer manufacture (06 10) is listed. However, these 4-digit entries only contain various minor entries.

Complete list of hazardous wastes listed under wastes from inorganic chemical processes (06) can be found in Appendix A.

Priority was given to 4-digit entry entries that include absolute entries. This is due to the fact that since inorganic chemical processes have wide range of applications it is difficult to estimate the total capacities of industries related to inorganic chemical processes. Moreover, it is difficult to gather information related to entries *metal containing wastes* (06 04), *sludges from on-site treatment* (06 05) and *wastes from inorganic processes not otherwise specified* (06 13).Consequently, in this thesis mfsu of acids, mfsu of bases and mfsu of halogens will be covered. Explosives manufacture is one of the areas where acids are being used in high amounts. For this reason, explosives manufacture is also covered in this chapter. Process descriptions of these processes are given in AppendixB-4. 7.4 Information Required for Determining Hazardous Wastes Generated from Inorganic Chemical Processes

Information required for determination of hazardous waste generation from organic chemical processes can be listed as follows:

- 1 Wastes from the mfsu of acids (06 01):
  - 1.1 **Types of acids produced and used in Turkey**: Currently, sulfuric acid, hydrochloric acid, phosphoric acid, nitric acid, boric acid and chromic acid are produced in Turkey.
  - 1.2 Production capacities of facilities producing each type of acid: Production capacities of facilities producing acids in Turkey are given in Table 7.1.

Producers	Location	Capacity (t/yr)	Production (t/yr)
Sulfuric acid production [48]			
BAĞFAŞ Bandırma Gübre Fabrikaları A.Ş.	Bandırma	500,000	500,000 *
TOROS GÜBRE Akdeniz Gübre Sanayii A.Ş[48]	Mersin	214,500	214,500 *
TÜGSAŞ Samsun Gübre Sanayii A.Ş. Nitric Acid II [49]	Samsun	214,500	**
KARADENİZ BAKIR İŞLETMELERİ	Samsun	282,920	282,920
ETİ BOR A.Ş: [50]	Bandırma	120,000	***
Elmadağ Barut Sanayii ve Ticaret A.Ş. BARUTSAN [51]	Ankara		730
PETKİM	İzmir		3,300
TOTAL			1,001,450
Hydrochloric acid production $\degree$			
PETKİM	İzmir		17,000 °°
Koruma Klor Alkali A.Ş.	İzmit	73,000	46,650 °°
AKKİM	İstanbul	50,000	47,600 °°
TOTAL			111,250
Phosphoric acid production			
BAĞFAŞ Bandırma Gübre Fabrikaları A.Ş.	Bandırma	150,000	150,000 *
GÜBRETAŞ	Yarımca	75,000	75,000 *

Table 7. 1: Acid production in Turkey

Producers	Location	Capacity (t/yr)	Production (t/yr)
Phosphoric acid production			
GÜBRETAŞ	İskenderun	75,000	75,000 *
TOROS GÜBRE	Mersin	71,000	71,000 *
Akdeniz Gübre Sanayii A.Ş. <sup>8</sup>	wichsin	71,000	/1,000
TÜGSAŞ			
Samsun Gübre Sanayii A.Ş.	Samsun	85,760	**
Phosphoric Acid I [49]			
TÜGSAŞ			
Samsun Gübre Sanayii A.Ş.	Samsun	108,800	282,920 *
Phosphoric Acid II [49]			
TOTAL			654,000
Nitric acid production [48]			
TOROS GÜBRE Akdeniz Gübre	Mersin	363,000	363,000
Sanayii A.Ş. [48]	wiersin	505,000	
TÜGSAŞ Kütahya Gübre Sanayii	Kütahya	26,700	**
A.Ş. Nitric Acid I	iiuuiiju	20,700	
			Diluted nitric
TÜGSAŞ Kütahya Gübre Sanayii	Kütahya	201,300	acid [52]: 1,760 Concentrated
A.Ş. Nitric Acid II	Itutuliyu	201,500	nitric acid
			[52]:103,700
TÜGSAŞ	Comlite	262,000	275 000 ***
Gemlik Gübre Sanayii A.Ş. [53]	Gemlik	363,000	275,000 ***
TOTAL			743,460
Boric acid production [50]			
ETİ Bor A.Ş.	Kütahya	100,000	1,500 *
ETİ Bor A.Ş.	Bandırma	85,000	89,600 *
TOTAL			91,100
Chromic acid production [54]			
Soda Sanayi A.Ş.	Mersin		160,000 *
Şişecam Company	101015111		100,000
TOTAL			160,000

## Table 7. 1 continued

\* Production in the year 2003 is given \*\* This plant was closed in 2003 \*\*\* This plant was closed in 2004

<sup>°°</sup> Information obtained from personal communication <sup>°°</sup> 2004 production

#### Waste generation factors related to acidic waste streams originating 1.3 from acid manufacture: In acid manufacturing processes no acidic

waste stream is generated. As a result, no waste generation factor is given in the literature for acidic waste streams from acid manufacturing processes.

1.4 **Capacities of facilities producing explosives**: The capacities of facilities producing explosives are given in Table 7. 2.

Producer	Products	Production Capacity (t/yr) [55]
	Nitroglycerine/Nitroglycol	182.5
	Black powder	400
Elmadağ Barut Sanayii	Trinitrotoluene (TNT)	6,570 [51]
ve Ticaret A.Ş.	Dinitrotoluene (DNT)	6,570 [51]
BARUTSAN	Sulphuric acid/Oleum	730 [51]
	Acid recovery	1.2 *
	Double base powder	182.5
Kırıkkale Nitroselüloz	Single and double base powders	
Ticaret ve Sanayii A.Ş.	Nitrocellulose	1,500 **
Nitromak Makine Kimya-Nitro Nobel	Emulsion explosives	7,500 **
Kimya Sanayii A.Ş.	ANFO	50,000 **
Orica-Nitro Patlayıcı	Emulsion explosives	6,000 **
Maddeler Sanayii ve Ticaret A.Ş.	ANFO	25,000 **

<b>Table 7. 2:</b>	Explosives	production	in	Turkey
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\* Acid recovery in 2002

<sup>\*</sup> Data obtained from personal communication

1.5 Waste generation factors related to acidic waste streams originating from each type of explosive produced: Waste generation factors need to be identified for different types of explosives since the types and amounts of wastes generated will differ from explosive to explosive. Waste generation factors related to acidic waste streams originating from explosives manufacture are given in Section 7.5.

### 2 Wastes from the mfsu of bases (06 02):

2.1 **Types of bases produced and used in Turkey:** Currently, sodium hydroxide and calcium hydroxide is being produced in Turkey.

2.2 **Production capacities of facilities producing each type of base:** A total of 3,837,000 t/yr of calcium hydroxide is produced in numerous facilities throughout Turkey. Sodium hydroxide production only occurs from chlorine production in Turkey. Currently, there are three Chlor-Alkali Plants in Turkey with a total alkali (sodium hydroxide) production capacity of 115,500 t/yr. Capacities of sodium hydroxide producing facilities is given in Table 7. 3.

Name of the Company	Location	Capacity (Chlorine) (t/yr) *	Capacity (Sodium hydroxide) (t/yr)
AKKİM	İstanbul	35,000	125,000
TARIM KORUMA	İzmit	36,500	40,150
PETKİM	İzmir	100,000	115,000
TOTAL		171,500	280,000

Table 7. 3: Chlor-Alkali Industry in Turkey

<sup>\*</sup> Information obtained from personal communication

- 2.3 Waste generation factors related to basic waste streams originating from each type of base manufactured: As in the case of acids, no basic waste stream is generated from base production. No waste generation factor is encountered in the literature regarding basic waste streams from base production.
- 3 Wastes from the mfsu of halogens and halogen chemical processes (06 07):
  - 3.1 **Types of halogens produced and used in Turkey:** The only type of halogen produced in Turkey is chlorine.
  - 3.2 **Production capacities of facilities producing chlorine:** Chlorine production capacities of chlor-alkali plants are given in Table 7. 3. All the other plants which were previously functional have been closed down during the last 5-10 years.
  - 3.3 Waste generation factors related to chlorine production: Spent acids are produced as a result of chlorine production. According to Reference Document on Best Available Techniques in the Chlor-Alkali Manufacturing Industry, hydrochloric acid is used in regeneration of ion exchange resins, for dechlorination and to adjust pH of cells and reduce

undesirable products in chlorine and sulfuric acid is used for drying of chlorine [64]. The spent acid usually becomes a waste product or requires reprocessing if it is reused [64]. If spent acids become a waste product rather than being re-used to control pH or returned to supplier for refortification, they fall into the entry *06 07 04* as hazardous wastes. Given that only membrane processes are used in Turkey, no other types of wastes are produced in significant amounts. Waste generation factors related to acid generation from chlorine production are given in Section 7.5.

# 7.5 Waste Generation Factors for Inorganic Chemical Processes

#### • Waste generation factors for mfsu of acids:

Waste generation factors for acid production: Although no acidic waste stream originates from acid manufacture, spent catalysts are generated from sulfuric acid production. According to Draft Reference Document on Best Available Techniques in Large Volume Organic Chemicals, Ammonia, Acids and Fertilizers Industries the amount of spent catalyst generated is 10 g/ton of H<sub>2</sub>SO<sub>4</sub> [57].

#### • Waste generation factors for explosives manufacture:

- Waste generation factors for DNT and TNT production: Typical wastewater generation rates for batch process is 0.093 m<sup>3</sup>/kg of TNT produced [60].
- Waste generation factors for nitrocellulose production: One estimate of the quantities of waste is that from manufacturing 45,350 kg of nitrocellulose gives 45,588 kg of mixed acids. Therefore, yielding to approximately 1 kg or mixed acids per kg of nitrocellulose produced.
- Waste generation factors for nitroglycerine production: Waste generation factor for wastewaters originating from nitroglycerine production is in the range of 151.5 – 643.5m<sup>3</sup>/d leading to 55,300 – 235,000m<sup>3</sup>/yr [61].
- Waste generation factors for smokeless powder production: In single base smokeless powder production preliminary step is

the production of nitrocellulose whereas, in double base smokeless powder there are two preliminary steps namely, production of nitrocellulose and nitroglycerine. Therefore, for single base powder production waste generation factors for nitrocellulose and for double base powder production waste generation factors for nitrocellulose and nitroglycerine will be used since no specific waste factor is given for smokeless powder production in the literature.

- Waste generation factors for mfsu of bases: No significant hazardous wastes are produced from base manufacture.
- Waste generation factors for mfsu of halogens: According to Reference Document on Best Available Techniques in the Chlor-Alkali Manufacturing Industry, 20 – 30 kg of hydrochloric acid/ton of chlorine and 15 - 20 kg of sulfuric acid/ton of chlorine is consumed [64]. Aside from this, no other hazardous waste stream is specified.
- 7.6 Hazardous Waste Generation from Inorganic Chemical Processes

# • Hazardous waste generation as a result of mfsu of acids:

• Hazardous waste generation as a result of acid manufacture: Except for the spent catalyst generated in sulfuric acid production no significant hazardous waste stream originated from acid manufacture. The amount of spent catalyst generated from sulfuric acid production is given in Table 7. 4.

Producer	Sulfuric acid production (t/yr)	Amount of spent catalyst generated (t/yr)
BAĞFAŞ Bandırma Gübre Fabrikaları A.Ş.	500,000	5
TOROS GÜBRE Akdeniz Gübre Sanayii A.Ş.	214,500	2.14
KARADENİZ BAKIR İŞLETMELERİ	282,920 *	2.82
PETKİM	3,300	Negligible
Elmadağ Barut Sanayii ve Ticaret A.Ş. BARUTSAN	730	Negligible
TOTAL		10

Table 7. 4: Spent catalyst from sulfuric acid production

\* 2005 production is around 130 000 tons.

- Hazardous waste generation as a result of explosives manufacture:
  - Hazardous waste generation from DNT and TNT manufacture: Typical wastewater generation rates for batch process is 0.093 m<sup>3</sup>/kg of TNT produced [60]. Given that 6,570 t/yr of TNT is produced in Turkey total wastewater generation from TNT production is 627,750 m<sup>3</sup>/yr. However, this amount of hazardous waste generation is not realistic. For this purpose direct information from Barutsan is obtained. According to Barutsan hazardous liquid waste emission is 2.17 L/sec which is equal to 68,400 m<sup>3</sup>/yr.
  - Hazardous waste generation from nitrocellulose manufacture: Nitrocellulose production of 1,500 tons/yr in Turkey yields to approximately 1,500 tons/yr of acidic wastewater.
  - Hazardous waste generation from nitroglycerine manufacture: Acidic wastewater flow rate changes between 151.4 – 643.5 m<sup>3</sup>/d for nitroglycerine production which is applicable to Turkey. Assuming the density of wastewater as 1 ton/m<sup>3</sup> above waste generation factor yields to 55,300 – 235,000 t/yr of waste production.
  - Hazardous waste generation from smokeless powder manufacture: As mentioned earlier acidic waste streams in production of smokeless powders consists only those originate from production of nitroglycerine and nitrocellulose. Therefore, no calculations are made for smokeless powder production other than those done for nitroglycerine and nitrocellulose.

Hazardous waste generation from explosives manufacture is summarized in Table 7.5.

Product	<b>Production in Turkey (t/yr)</b>	Acidic wastes produced (t/yr)
DNT/TNT	6,570	70,000
Nitrocellulose	1,500	1,500
Nitroglycerine	182.5	55,300 - 235,000
TOTAL		125,300 - 306,500

Table 7. 5: Total acidic wastes produced in Turkey as a result of explosives manufacture

- Hazardous waste generation as a result of mfsu of bases: No significant hazardous waste streams originating from mfsu of bases could be identified.
- **Hazardous waste generation as a result of mfsu of halogens**: The amount of hazardous wastes generated from chlorine production is given in Table 7. 6. As mentioned before spent acid from chlorine production has potential to be hazardous waste if not re-used or sent to the supplier for further processing.

Name of the Company	Capacity (Chlorine) (ton/yr)	HCl consumption (ton/yr)	H <sub>2</sub> SO <sub>4</sub> consumption (ton/yr)
AKKİM	35,000	700 - 1,050	525 - 700
TARIM KORUMA	36,500	730 – 1,095	550 - 730
PETKİM	100 000	2,000 - 3,000	1,500 - 2,000
TOTAL		3,430 - 5,145	2,575 - 3,430

Table 7. 6: Spent acid generation from chlorine production

Results of this chapter are summarized in Table 7.7.

#### 7.7 Comments

There is always a risk of accidental pollution and leakages when chemicals are produced and handled. However, these accidental spills and leaks cannot be estimated by waste generation factors [57]. This is valid for production of all acids.

Since boric acid production is not widespread across the world, wastes generated as a result of boric acid production will be based on case studies. Although, Reference Documents published by European Commission does not cover boric acid production, there are two case studies in USA. Research about capacities or production data was undertaken however, no results were obtained. However, it was not possible to develop waste generation factors for boric acid production due to lack of information on capacities of these two facilities. In order to determine the amount of hazardous wastes generated as a result of boric acid production in Turkey it is strictly necessary to conduct studies in association with Turkish boric acid producer ETI BOR.

Gypsum is a by-product in wet phosphoric acid production; and it is stated that for every ton of phosphoric acid ( $P_2O_5$ ) produced around 4 – 5 ton of gypsum are

	Name of the entry		Amou	nt generated	(t/yr)
2-digit	4-digit	6-digit	6-digit	4 digit	2 digit
		Sulfuric acid and sulfurous acid (06 01 01)			
		Hydrochloric acid (06 01 02)			
	Wastes from mfsu of acids	Hydrofluoric acid (06 01 03)		125,300	
	(06 01)	<i>Phosphoric acid and phosphorous</i> <i>acid (06 01</i>			
		Nitric acid and nitrous acid (06 01 05)			
		<i>Other acids (06 01 06)</i>			
	Wastes from mfsu of bases (06 02)	Calcium hydroxide (06 02 01)			131,300 – 315,000
Wastes from		Ammonium hydroxide (06 02 03)			
Inorganic Chemical		Sodium and potassium hydroxide (06 02 04)			
Processes(06)		<i>Other bases (06 02 05)</i>			
		Solid salts and solutions containing cyanides (06 03 11)			
	Wastes from mfsu of salts and their solutions and metallic oxides (06 03)	Solid salts and solution containing heavy metals (06 03 13)			
	metallic oxides (00 03)	Metallic oxides containing heavy metals (06 03 15)			
	Metal containing wastes	Wastes containing arsenic (06 04 03)			
	8	Wastes containing mercury (06 04 04)			
	other than those mentioned in 06 03 (06 04)	Wastes containing other heavy metals (06 04 05)			

# Table 7. 7: Results obtained for Wastes from Inorganic Chemical Processes (06)

	Name of the entry			Amount generated (t/yr)		
2-digit	4-digit	6-digit	6-digit	4 digit	2 digit	
	Sludges from on-site effluent treatment (06 05)	Sludges from on-site effluent treatment containing dangerous substances (06 05 02)				
	Wastes from mfsu of sulfur chemicals, sulfur chemical processes and desulphurization processes (06 06)	Wastes containing dangerous sulfides (06 06 02)				
Wasterfusio	Wastes from the mfsu of halogens and halogen chemical processes (06 07)	Wastes containing asbestos from electrolysis (06 07 01)				
Wastes from Inorganic Chemical		Activated carbon from chlorine production (06 07 02)		6,000 -		
Processes(06)		Barium sulfate sludge containing mercury (06 07 03)		8,575		
		Solutions and acids (06 07 04)	6,000 – 8,575			
	Wastes from the mfsu of silicon and silicon derivatives (06 08)	Wastes containing dangerous silicones (06 08 02)				
	Wastes from the mfsu of phosphorus chemicals and phosphorous chemical processes (06 09)	Calcium-based reaction wastes containing or contaminated with dangerous substances (06 09 03)				

# Table 7. 7 continued

	Name of the entry			Amount generated (t/yr)		
2-digit	4-digit	6-digit	6-digit	4 digit	2 digit	
	Wastes from mfsu of nitrogen chemicals, nitrogen chemical processes and fertilizer manufacture (06 10)	Wastes containing dangerous substances (06 10 02)				
	Wastes from inorganic	Inorganic plant protection products, wood-preserving agents and other biocides (06 13 01)				
	chemical processes not	Spent activated carbon (06 13 02)				
	otherwise specified (06 13)	Wastes from asbestos processing (06 13 04)				
		Soot (06 13 05)				

Table 7. 7 continued

produced. Due to impurities that may be present in the raw materials and possibility of the presence of radioactive components the gypsum generated as a result of phosphoric acid production need to be analyzed to assess the possibility of being hazardous [57].

No reference that contains waste generation factors regarding chromic acid production could be found. Due to the lack of information regarding chromic acid production wastes, direct information was tried to be obtained. According to KROMSAN A.Ş. no hazardous waste streams are being generated throughout the process. Since no other facility that produces chromic acid exists in Turkey and no literature values regarding waste factors this information could not be verified.

Spent activated carbon from chlorine production is listed among absolute entries in EWC and Annex 7 of RCHW of Turkey. No waste generation factor could be obtained regarding waste activated carbon from chlorine production. For this reason, direct information is tried to be obtained. All the producers stated that there is no activated carbon wasted throughout their processes.

### **CHAPTER 8**

# WASTES FROM ORGANIC CHEMICAL PROCESSES

#### 8.1 Objective and Scope

Objective of this chapter is to determine the amount of hazardous wastes originating from organic chemical processes. According to EWC and Annex 7 of RCHW of Turkey organic chemical processes cover mfsu of basic organic chemicals, plastics, synthetic rubber and man-made fibers, organic dyes and pigments, organic plant protection products, wood preserving agents and other biocides, pharmaceuticals, fats, grease, soaps, detergents, disinfectants and cosmetics, fine chemicals and chemical products not otherwise specified.

#### 8.2 Introduction

According to U.S. Census Bureau basic organic chemicals manufacturing whose wastes are covered under the entry of 07 01 are described as manufacturing aromatic petrochemicals from refined petroleum or natural gas, manufacturing aromatic petrochemicals from by refining crude petroleum, manufacturing organic industrial gases, manufacturing synthetic organic dyes and pigments, manufacturing ethyl alcohol, manufacturing organic insecticidal, herbicidal, fungicidal, pesticidal preparations, manufacturing elastomeres, manufacturing urea, manufacturing natural glycerine, and manufacturing natural food colorings [93]. Therefore, 07 01 also covers subsequent entries.

Plastics and synthetic rubbers are produced in petrochemical complexes. Production of many different plastics in petrochemical plants occurs through various processes starting from conversion of naphtha to ethylene that is a common raw material used in processes. Organic dyes and pigments are not currently being manufactured in Turkey. Production only occurs from formulation of organic dyes and pigments. Pharmaceuticals manufacture involves a variety of production processes. As a result of these processes many different pharmaceutical products are being manufactures which have different constituents and properties.

Although ingredients may be variable fats, grease and soaps are being produced by similar processes. However, production of detergents, disinfectants and cosmetics show great variation due to presence of different substances and raw materials within the products.

Fine chemicals described as the group of organic substances including organic dyes and pigments, active pharmaceutical ingredients, vitamins, biocides and plant health products, fragrances and flavors, optical brighteners, flame-retardants, plasticizers and explosives.

8.3 Hazardous Wastes Generated as a Result of Organic Chemical Processes

Hazardous waste generation from organic chemical processes is covered under *wastes from organic chemical processes (07)* in EWC and Annex 7 of RCHW of Turkey [3,19]. Under 07 both absolute and minor entries are found. These entries are presented in Appendix A. Absolute entries common for all 4-digit entries include:

- o aqueous washing liquids and mother liquors
- o organic halogenated solvents, washing liquids and mother liquids
- o other organic solvents, washing liquids and mother liquors
- o halogenated still bottoms and reaction residues
- o other still bottoms and reaction residues
- o halogenated filter cakes and spent absorbents
- and other filter cakes and spent absorbents [3,19]
   Minor entries include:
- o sludges from on-site treatment containing dangerous substances,
- o wastes from additives containing dangerous substances
- o wastes containing dangerous silicons and
- o solid wastes containing dangerous substances [3,19].

8.4 Information Required for Determining Hazardous Wastes Generated from Organic Chemical Processes

Information required for determination of hazardous waste generation from organic chemical processes can be listed as follows:

- 1 Wastes from mfsu of plastics, synthetic rubber and man-made fibers:
  - 1.1 Facilities producing plastics, synthetic rubber and man-made fibers in Turkey: There are currently three facilities producing materials that can be categorized as plastics, synthetic rubber and man-made fibers. These facilities are PETKİM in İzmir, TÜPRAŞ in İzmit and Başer Kimya in İstanbul.
  - 1.2 Types of plastics, synthetic rubber and man-made fibers produced in Turkey: Types of plastics, synthetic rubber and man-made fibers produced in these facilities are given in Table 8. 1.

Name of the company	Production plants			
	Ethylene			
	Low Density	Polyethylene (LDPE)		
	High Density (HDPE)	y Polyethylene		
PETKİM [65]		Benzene		
	Aromatics	Orthoxylene		
		Paraxylene		
	Ethylene gly	Ethylene glycol (mono)		
	Acrylonitrile	;		
	VCM			
	PVC			
	Polypropyler	ne (PP)		
	Polybutadier	ne Rubber		
TÜPRAŞ [67]	Styrene Buta	diene Rubber		
	Polystyrene			
BAŞER Kimya [66]	Polystyrene			

 Table 8. 1: Types of materials produced in petrochemical plants

1.3 Capacity information for each type of plastic, synthetic rubber and man-made fibers: Capacities of different production processes used in petrochemical plants in Turkey are given in Table 8.2.

Name of the company	Prod	Capacity (t/yr)	
	Ethylene		400,000
	Low Density Po	olyethylene (LDPE)	190,000
	High Density P	olyethylene (HDPE)	96,000
PETKİM [65]		Benzene	123,000
		Orthoxylana	46,000
	Aromatics	Orthoxylene	[66]
		Paraxylene	119,000
		raraxytene	[66]
	Ethylene glycol	89,000	
	Acrylonitrile	90,000	
	VCM	142,000	
	PVC	150,000	
	Polypropylene	80,000	
	Polybutadiene Rubber		20,000
TÜPRAŞ [67]	Styrene Butadie	ene Rubber	33,000
	Polystyrene	15,000	
BAŞER Kimya [66]	Polystyrene	40,000	

Table 8. 2: Capacities of production plants in petrochemical industry in Turkey

Waste generation factors for manufacture of plastics, synthetic 1.4 rubber and man-made fibers: In the literature waste generation factor for production of plastics, synthetic rubber and man-made fibers are expressed. Waste generation factors related to hazardous wastes should be identified by referring to the generic types of hazardous wastes listed in EWC and Annex 7 of RCHW. Moreover, terminology used in literature and in EWC is different. For this reason, wastes for which waste generation factors are given for should be classified according to EWC.

### 2 Wastes from mfsu of organic dyes and pigments:

Facilities producing and using organic dyes and pigments in Turkey: 2.1 In Turkey production of organic dyes and pigments occurs only from formulation of concentrated organic dyes and pigments exported abroad. The large application areas of organic dyes and pigments prevent from identifying the sources in which organic dyes and pigments are used.

- 2.2 **Number of facilities formulating organic dyes and pigments:** The number of plants formulating and using organic dyes and pigments could not be found. For this reason no further calculation could be done.
- 2.3 Capcity of facilities formulating different types of organic dyes and pigments
- 2.4 Waste generation factor regarding formulation of different types of organic dyes and pigments:
- 3 Wastes from mfsu of pharmaceuticals
  - 3.1 **Facilities producing pharmaceuticals:** Information about pharmaceutical products is available.
  - 3.2 Number of pharmaceutical production plants
  - 3.3 **Processes applied in pharmaceutical production plants:** Due to variable products processes applied in each plant for each product could not be identified. For this reason not further calculation could be done.
  - 3.4 Capacities of each process applied in pharmaceutical industry in Turkey
  - 3.5 Waste generation factors developed for each process of pharmaceutical production
- 4 Wastes from mfsu of fats, grease, soaps, detergents, disinfectants and cosmetics
  - 4.1 Facilities producing, formulating and using fats, grease, soaps, detergents, disinfectants and cosmetics: As in the case of organic dyes and pigments production, formulation and use of fats, grease, soaps, detergents, disinfectants and cosmetics involve high number of facilities. Therefore, these facilities could not be identified. No calculations could be done these industrial sectors.

- 4.2 Number of facilities producing, formulating and using fats, grease, soaps, detergents, disinfectants and cosmetics
- 4.3 Capacities of facilities producing, formulating and using fats, grease, soaps, detergents, disinfectants and cosmetics
- 4.4 Waste generation factors related to production, formulation and use of fats, grease, soaps, detergents, disinfectants and cosmetics
- 8.5 Hazardous Waste Generation Factors for Wastes from Organic Chemical Processes

Waste generation factors found for *wastes from organic chemical processes* (07) is given below:

• Waste generation factors for manufacture of plastics, synthetic rubber and man-made fibers: Waste generation factors for manufacture of plastics, synthetic rubber and man-made fibers are summarized in Table 8. 3.

Production	Wastewater		Solids	wastes
process	Quantity	Properties	Quantity	Properties
Ethylene Cracking [69]	Process water: <b>0.03 – 2 m<sup>3</sup>/t</b> ethylene		Organic sludges: <b>1.03</b> – <b>5.24 kg/t</b> ethylene Spent catalysts: <b>0.159</b> – <b>1.054 kg/t</b> ethylene	Total quantity : <b>0.05 – 6 kg/t</b> of ethylene
	Total aqueous effluent stream: 1 – 4 m <sup>3</sup> /t ethylene		Spent adsorbents Coke: <b>0.255</b> – <b>7.954 kg/t</b> ethylene	
LDPE [68]			4.6 kg/t product	Hazardous wastes
HDPE [68]			3.9 kg/t product	Hazardous wastes
Aromatics Production [69]				

 Table 8. 3: Waste generation factors for plastics and synthetic fiber production [68]

Production	Wastew	ater	Solids w	vastes
process	Quantity	Properties	Quantity	Properties
	Effluent from ethylene oxide recovery section: <b>200 –</b>		Effluent from ethylene oxide recovery section: <b>0.5 –</b> <b>10 kg/t</b> EO Heavy glycols:	
EG/EO [69]	2,300 kg/t EO		<b>2 – 100 kg /t</b> EO	
	Process effluents: <b>450</b> – <b>1 100 kg/t</b> EO		Catalyst <b>: 0.12</b> – <b>0.8 kg/t</b> EO	Catalysts are changed every 1 to 4 years.
Acrylonitrile [69]	Quench effluent stream: <b>350 –</b> <b>900 kg/t</b> ACN Stripper bottoms: <b>500 -</b> <b>2,000 kg/t</b> ACN Hydrogen cyanide: <b>90 -</b> <b>120 kg/t</b> ACN Acetonitrile: <b>5</b> <b>– 32 kg/t</b> ACN Ammonium sulphate: <b>115 –</b> <b>200 kg/t</b> ACN		Waste catalyst: <b>0.3 – 0.7 kg/t</b> ACN	
VCM [69]	Liquid residues <b>: 25 –</b> <b>40 kg/t</b> VCM	Typically contains more than 60% chlorine. Usually recovered.	Spent oxychlorination catalyst: 10 – 200 g/t VCM Direct chlorination residue: 10 – 50 g/t VCM	Contains
			Coke: <b>0.1 – 0.2</b> <b>kg/t</b> of VCM	residual chlorinated HCs

Table 8. 3 continued

Production	Waste	water	Solids v	wastes
process	Quantity	Properties	Quantity	Properties
	Emulsion process	Total VCM emissions: <b>59 g/t</b> Hazardous waste: <b>120</b>		
PVC [68]	Suspension process	g/tTotal VCMemissions:1,200 g/tHazardouswaste:1,200 g/t		
Polypropylene[68]	3.9 kg/t product	Hazardous wastes		
Polystyrene [68]	Wastewater: <b>1.1 t/t</b> polystyrene Cooling tower purge water: <b>0.5 t/t</b> polystyrene		Solid waste: <b>0.6 kg/t</b> polystyrene	Hazardous wastes
Styrene Butadiene Rubber [68]	Hazardous waste: <b>3.0</b> kg/t SRB Non- hazardous waste: <b>0.24</b> kg/t SBR	-	Rubber waste: 1.5 kg/t SBR	
Polybutadiene Rubber [68]			Rubber waste: <b>1.2 kg/ t</b> product	

Table 8. 3 continued

Hazardous waste generation as a result of manufacture of plastics, synthetic rubber and man-made fibers: Waste generation in petrochemical industry is given in Table 8. 4. Wastes identified as hazardous are given in Table 8. 5 as a total on product basis. Lastly, hazardous waste generation from manufacture of plastics rubber and man-made fibers are given in Table 8. 6.

<sup>8.6</sup> Hazardous Waste Generation from Organic Chemical Processes

Name of the	e Production plants production		Current production			Hazardous waste production (t/yr)			
company			(t/yr)	Liquid	Solid	Liquid	Solid		
	Ethylene		Ethylene		376,000	Process water: 12,000 – 752,000	Organic sludges: 390–1,970 Spent catalysts: 60 – 400		Organic sludges: 390–1,970 Spent catalysts: 60 – 400
				Total aqueous effluent stream: 376,000 – 1,504,000	Coke: 100 – 2,990				
	(LDPE)		191,000		880		880		
	(HDPE)		90,240		350		350		
PETKİM		Benzene	131,610						
[65]	Aromatics	Orthoxylene	13,960						
		Paraxylene	96,985						
	Ethylene		00.770	Effluent from ethylene oxide recovery section: 16,500 – 190,400	Effluent from ethylene oxide recovery section: 40 - 830				
	glycol (mono)		82,770	Process effluents: 37,300	Heavy glycols: 165 - 8,300				
				- 91,000	Spent catalyst: 10– 70		Spent catalyst: 10–70		

 Table 8. 4: Waste generation from petrochemical industry in Turkey

# Table 8. 4 continued

Name of	Production	Current	Waste production (t/yr)		Hazardous waste production (t/yr)		
the company	plants	production (t/yr)	Liquid	Solid	Liquid	Solid	
	VCM	140,580	Liquid residues: 3,500 – 5,600	Spent oxychlorination catalyst: 1,5 – 30	Liquid residues: 3,500 – 5,600	Spent oxychlorination catalyst: 1,5 – 30	
			Process effluents: 37,300 – 91,000	Direct chlorination residue: 1.5 – 7		Direct chlorination residue: 1.5 – 7	
	Polypropylene (PP)	77,600	Hazardous waste: 300	Coke: 15 – 30	Hazardous waste: 300		
PETKİM [65]	Acrylonitrile	88,200	Quench effluent stream: 31,000 – 80,000 Stripper bottoms: 44,000 - 176,400 HCN: 8,000 – 10,500 Acetonitrile: 440 – 2,800 Ammonium sulfate: 10,150 – 17,600	Waste catalyst: 30 – 60	Quench effluent stream: 31,000– 80,000 Stripper bottoms: 44,000 -176,400 HCN: 8,000 – 10,500 	Waste catalyst: 30 – 60	

Name of Production		Current Waste product		on (t/yr)	Hazardous waste production (t/yr)	
the company	plants	production (t/yr)	Liquid	Solid	Liquid	Solid
PETKİM	DVC	156,000	Total VCM emissions: 190		Total VCM emissions: 190	
[65]	PVC	156,000	Hazardous wastes: 190		Hazardous wastes: 190	
	Styrene		Hazardous waste. 85	Rubber waste:	Hazardous waste. 85	
TÜPRAŞ	Butadiene 27,7 Rubber	27,720	Non-hazardous waste: 7	42		
[67]	Polystyrene	10,950	Wastewater: 12,000	Solid waste: 6.5		
			Cooling tower purge: 5,500			Solid waste: 6.5
BAŞER Kimya [61]	Polystyrene	40 000	Wastewater:44,000	Solid waste: 25		
			Cooling tower purge: 20,000			Solid waste: 25

Table 8. 4 continued

<b>D</b> 114	Decile of an Decourse	Calculated Va	I		
Facility	<b>Production Process</b>	Liquid wastes	Solid wastes	- Entry	
	Ethylona		450 2 270	07 02 08	
	Ethylene		450 - 2,370	16 08 07	
	LDPE		880	07 08 02	
	HDPE		350	07 08 02	
	Ethylene glycol		10-70	16 08 07	
				07 02 01	
	Acrylonitrile	83,000 -	27 – 62	07 02 08	
	Actylointine	265,100	27 - 02	06 01 06	
PETKİM				16 08 07	
		3,500 - 5,600		07 02 08	
	VCM		3 - 37	16 08 07	
	V CIVI			07 02 07	
				07 02 07	
	PVC	380		07 02 07	
	PP	300		07 02 08	
	TOTAL	120,000 -	1700 - 3770		
	TOTAL	271,400	1700 5770		
	Styrene Butadiene	85			
	Rubber			07 02 08	
TÜPRAŞ	Dolucturono		6.5	07 02 08	
	Polystyrene TOTAL	85	<u>6.5</u> 6.5	07 02 08	
DACER	IUIAL	6.5	0.3		
BAŞER Kimya	Polystyrene		25	07 02 08	
TOTAL		120,000 – 271,500	1730 - 3800		

Table 8. 5: Total amount of hazardous wastes produced by petrochemical industry in Turkey

# 8.7 Comments

An important problem encountered throughout the calculated of wastes from organic chemicals is the difference in terminology of different references. Wastes given in

Table 8. 4 need to be studied in order to be able to understand under which code they fall in. since classification given in EWC and wastes types given in Draft Reference Document on Best Available Techniques in Production of Polymers are different from each other.

	Name of the entry	Amount generated (t/yr)			
2-digit	4-digit	6-digit	6-digit	4 digit	2 digit
	Wastes from mfsu of basic organic chemicals (07 01)				
		Aqueous washing liquids (07 02 01)	31,000– 80,000		
		Organic halogenated solvents, washing liquids and mother liquids (07 02 03)			
	Wastes from mfsu of plastics, synthetic rubber and man-made fibers (07 02)	Other organic solvents, washing liquids and mother liquids (07 02 04)			112,380  316,400
		Halogenated still bottoms and reaction residues (07 02 07)	380 - 400	112,380	
Wastes from		Other still bottoms and reaction residues (07 02 08)	81,000 – 236,000	316,400	
Organic Chemical		Halogenated filter cakes and spent absorbents (07 02 09)			
Processes(07)		Other filter cakes and spent absorbents (07 02 10)			
		Sludges from on-site effluent treatment containing dangerous substances (07 02 11)			
	Wastes from mfsu of organic dyes and pigments(07 03)				
	Wastes from mfsu of organic plant production products, wood preserving agents and other biocides (07 04)				
	Wastes from mfsu of pharmaceuticals (07 05)				
	Wastes from mfsu of fats, grease, soaps, detergents, disinfectants and cosmetics (07 06)				

# Table 8. 6: Results obtained for wastes from organic chemical processes (07)

# **CHAPTER 9**

# WASTES FROM THERMAL PROCESSES

#### 9.1 Objective and Scope

Objective of this chapter is to determine the amount of hazardous wastes generated as result of thermal processes. In EWC and Annex 7 of RCHW of Turkey thermal processes include power stations and other combustion plants, iron and steel industry, aluminum, lead, zinc, copper, silver, gold, platinum and other non-ferrous thermal metallurgy, casting of ferrous and non-ferrous pieces, manufacture of glass and glass products, manufacture of ceramic goods, bricks, tiles and construction products and finally, manufacture of cement, lime, and plaster and articles and products made from them.

### 9.2 Introduction

Power stations make use of combustion chambers for generation electricity. Coal, lignite, liquid fuels and natural gas can be used in power stations as fuels.

Thermal metallurgy of metals can be separated into two categories. The first one is the primary production in which concentrates from extraction and beneficiation of raw ores are processed. The second category is secondary production in which recycled materials or minerals are processed.

## 9.3 Hazardous Wastes Generated as a Result of Thermal Processes

Wastes listed under wastes from thermal processes (10) are wastes from power stations and other combustion plants (10 01) wastes from iron and steel industry (10 02) wastes from aluminum thermal metallurgy (10 03) wastes from lead thermal metallurgy (10 04) wastes from zinc thermal metallurgy (10 05) and wastes from copper thermal metallurgy (10 06)

In this thesis are wastes from power stations and other combustion plants (10 01), wastes from aluminum thermal metallurgy (10 03), wastes from lead thermal metallurgy (10 04), wastes from zinc thermal metallurgy (10 05), wastes from copper thermal metallurgy (10 06). Main reason for concentrating on these entries was that these entries contain 6-digit absolute entries [3,19].

Hazardous wastes that can be originating from power stations and other large combustion plants listed as absolute entries are *oily fly ash and boiler dust (10 01 04), sulfuric acid (10 01 09)* and *fly ash from emulsified hydrocarbons used as fuel (10 01 13)*. Among minor entries one important minor entry is *wastes from gas-cleaning containing dangerous substances (10 01 18)* [3,19].

Primary and secondary production slags from (10 03 04, 10 03 08, 10 04 01, 10 08 08) dross and skimmings (10 03 09, 10 04 02) are among the absolute entries listed in EWC and Annex 7 of the RCHW for wastes from aluminum thermal metallurgy (10 03) and wastes from lead thermal metallurgy (10 04). Other than these common entries among wastes from thermal metallurgy processes are flue gas dust (10 04 04, 10 05 03, 10 06 03), solid wastes from gas treatment (10 04 06, 10 05 05, 10 06 06), sludges and filter cakes from gas treatment (10 04 07, 10 05 06, 10 06 07), calcium arsenate (10 04 03) and other particulates and dusts (10 04 05) [3,19].

9.4 Information Required for Determining Hazardous Wastes Generated from Thermal Processes

Information required for determination of hazardous waste generation from thermal processes can be listed as follows:

- **1** Wastes from power stations and other combustion plants (10 01):
  - 1.1 **Power stations that have flue gas desulphurization (FGD) system:** Currently 7 thermal power plants, given in Table 9. 1 along with capacities, have flue gas desulphurization systems [70].
  - 1.2 **Capacities of power stations that have FGD systems**: In Table 9. 1, capacities of power stations that have FGD systems are given.

Power Plant	Location	Capacity [70]
Çayırhan	Ankara [72]	2 x 150 MW 2 x 160 MW
Orhaneli	Bursa [71]	1 x 210 MW
Afşin- Elbistan	K.Maraș [71]	4 x 360 MW
Kemerköy	Muğla [73]	3 x 210 MW
Yatağan	Muğla [73]	3 x 210 MW
Kangal	Sivas [71]	1 x175 MW
İsken	İskenderun	1320 MW

Table 9. 1: Thermal power plants that have FDG system

\* Wet basis

Average value for Adana and Kahramanmaraş district

Average value for Central Anatolia District

Sulfur content of coal or lignite used in power plants that has FGD 1.3 systems: Throughout the calculations, it is assumed that FGD wastes are proportional to the sulfur content of feed material. Information about sulfur contents of coal burned in each power station that has FGD system is found.

Table 9. 2: Sulfur contents of coal or lignite being burned in power stations having FGD systems

Power Plant	Location	Sulfur Content (%) [71]
Çayırhan	Ankara [72]	3.86 *
Orhaneli	Bursa [71]	1.64 *
Afşin- Elbistan	K.Maraş [71]	2.0 **
Kemerköy	Muğla [73]	1.33 *
Yatağan	Muğla [73]	2.57 *
Kangal	Sivas [71]	3.2 ***
İsken	İskenderun	0.6 - 0.8

\*\*\* Average value for Adana and Kahramanmaraş district \*\*\*\* Average value for Central Anatolia District

1.4 Waste generation factors regarding FGD wastes: Waste generation factor is required to determine the amount of FGD wastes. Development of waste generation factor for FGD waste is discussed in Section 9.5.

- 2 Wastes from aluminum thermal metallurgy (10 03):
  - 2.1 **Capacity of primary and secondary aluminum production accomplished by thermal processes**: The only primary aluminum production facility in Turkey is Seydişehir Aluminum Production Facility of ETİ Bank A.Ş. Production of this facility for the period of 1975 to 2002 is given in Table 9. 3.

Year	<b>Production (Tons)</b>	Year	<b>Production (Tons)</b>
1975	18 149	1990	58 564
1976	37 508	1991	55 802
1977	51 331	1992	58 581
1978	32 288	1993	58 501
1979	31 720	1994	59 754
1980	33 574	1995	61 531
1981	39 985	1996	62 100
1982	36 521	1997	62 020
1983	30 381	1998	61 803
1984	37 887	1999	61 705 <sup>3</sup>
1985	54 150	2000	61 501 <sup>3</sup>
1986	60 003	2001	61 730 <sup>3</sup>
1987	41 685	2002	62 501 <sup>3</sup>
1988	56 500		
Avera	Average production		61 314 t/yr

 Table 9. 3: Production of primary aluminum in Seydişehir Aluminum Production Facility [74]

Unfortunately, capacity information could be reach directly. However, according to the Chamber of Mining Engineers, secondary aluminum production originates mainly from small scale facilities and it is about 10% of the consumption in Turkey [75]. In Table 9. 4 consumption of aluminum in Turkey and approximate secondary aluminum production is given. Since secondary aluminum production is given directly and average value if calculated from the data given in Table 9. 4

2.2 Waste generation factors for hazardous wastes from both primary and secondary thermal aluminum production: In EWC and Annex 7 of RCHW of Turkey different wastes are listed as absolute or minor entries. Waste generation factors should be found for each of the wastes. These factors are given in Section 9.5 in more detail.
Year	Consumption (tons/yr)	Secondary Aluminum Production (tons/yr)
1994	115 200	11 520
1995	144 000	14 400
1996	136 000	13 600
1997	178 300	17 830
1998	180 700	18 070
1999	136 800	13 680
Average	148 500	14 850

Table 9. 4: Consumption of aluminum in Turkey and approximate secondary production [74]

# **3** Wastes from lead thermal metallurgy (10 04):

3.1 **Capacity of primary and secondary lead production in Turkey:** All related facilities in Turkey currently produce lead through secondary processes [74]. According to State Planning Organization, secondary lead production from scraps is as given in Table 9. 5.

 Table 9. 5: Secondary lead production in Turkey [28]

Year	1990	1991	1992	1993	1994	1995	1996	Average
Production (from scrap) (t/yr)	11,000	8,500	10,500		8,735	861	13,438	8,840

3.2 Waste generation factors for hazardous wastes from both primary and secondary thermal lead production: EWC and Annex 7 of RCHW contains numerous absolute entries under 10 04. Waste generation factors need to be identified for each of the wastes. Waste generation factors for lead thermal metallurgy are presented in Section 9.5.

# 4 Wastes from zinc thermal metallurgy (10 05):

- 4.1 **Capacity of primary and secondary zinc production in Turkey:** No pyrometallurgical zinc production occurs in Turkey.
- 4.2 Waste generation factors for hazardous wastes from zinc thermal lead production

#### 5 Wastes from copper thermal metallurgy (10 06):

5.1 Capacity of primary and secondary copper production in Turkey: Only blister copper producer in Turkey is Samsun facility of Karadeniz Bakır İşletmeleri A.Ş. which has a capacity of 38,760 tons/yr [74]. From the beginning of year 2005 until July, 19,000 tons of blister copper has been produced in Samsun facility. It is anticipated that annual production will be in the range of 30,000 – 32,000 tons in 2005. In this facility pyrometallurgical processes are used [75]. Six facilities in Turkey produce electrolytic copper. Capacities of these facilities are given in Table 9. 6.

Facilities	Location	Capacity(t/yr)
Sarkuysan	İstanbul	70,000
Özün Metal	İstanbul	36,000
Anadolu Bakır	Sakarya	20,000
Erbakır	Denizli	18,000
HES	Kayseri	25,000
Elbak	Kayseri	7,000
TOTAL		174,000

 Table 9. 6: Electrolytic copper producers in Turkey [75]

- 9.5 Hazardous Waste Generation Factors for Wastes from Thermal Processes
  - Waste generation factors for power stations: According to Draft Reference Document on Best Available Techniques for Large Combustion Plants for a 750 MW<sub>e</sub> power plant burning one million tones of coal with an ash content of e.g. 10% and sulfur content of e.g. 1%, some 154,000 tones of coal combustion products (CCPS) are yielded annually. Among this 154,000 CCPs 16 tones is bottom ash, 84,000 tones is fly ash and 54,000 tones is FGD-Gypsum [79]. Only gypsum is regarded as a minor entry hazardous waste in EWC [19]. This figure is for a plant with a full load of 6,000 hours. Assuming 24 hours operation, 6,000 hours means 250 days operation in a year. Therefore, for 365 days operation the amount of gypsum generated for 1% sulfur content is 78,840 tons/year. In the calculations it will be assumed that gypsum amount is directly proportional with sulfur content in the oil [79]. Therefore, waste generation

factor for gypsum is 0.288 ton/day/MW/% sulfur. Moreover,  $8.5 \times 10^{-3}$  ton/day/MW/% sulfur of bottom ash and 0.448 ton/day/MW/% sulfur of fly ash is produced.

- Waste generation factors for aluminum thermal metallurgy:
  - Waste generation factors for primary aluminum thermal processes: Red mud produced during the extraction of alumina from bauxite contains 3 to 12 kg of NaOH per ton of alumina produced [78]. This means that red mud can be classified as 06 02 04- sodium and potassium hydroxide [19].

With a cathode lifetime of 5 - 8 years, which is common for modern plants, the quantity of Spent Pot Lining (SPL) generated is 20 - 30 kg/t aluminum produced. SPL can be *16 11 03- other linings and refractories from metallurgical processes containing dangerous substances* [19].Skimmings from the holding and treatment processes represent 15 to 20 kg per ton of aluminum produced.

 Table 9. 7: Hazardous waste generation factors for primary aluminum production [78]

Source	Quantity (kg per ton of Al)		
Al skimmings	15 – 25		
SPL	20 - 30		
Red mud	3 - 12		
Other Hazardous Wastes	7 – 15		

• Waste generation factors for secondary aluminum thermal processes: Hazardous waste generation factors are given in Table 9. 8.

Table 9. 8: T	ypical residues	from secondary	aluminum	production [78]
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Residue	Origin	Volume
Salt slag	Melting in rotary drum	Up to 500 kg/t Al
		Up to 35 kg/t Al
Filter dust	Exhaust gas cleaning	(0.1 – 1.0 kg/t Al –using
		Closed Well furnace)
Furnace lining	Melting furnace	~2 kg/t Al
	All furnaces not using salt,	~25 kg/t Al
Skimmings	cleaning of smelter, foundaries	(40 – 80 kg/t Al –using
	cleaning of smeller, foundaries	Closed Well furnace)
Dust		300 – 700 kg/t

• Waste generation factors for lead thermal metallurgy: It is known that lead production in Turkey exclusively occurs by secondary processes. In Table 9. 9, waste generation factors for various processes are given. Information related to types of processes applied for secondary lead thermal metallurgy could not be found on facility basis. For this reason, waste generation factors are found for slag, dross and flue dust covering all the processes. Waste factors for slag, dross and flue dust are developed by averaging waste generation factors for different processes. These average waste factors are given in Table 9. 9.

Production step	Production or residue	Quantity (kg/t Pb)				
Slag Fuming Plant						
	Slag	700				
Slag fuming	Matte	2.5 - 25				
	Steam	2,500				
Battery process- Short	rotary					
	$Na_2SO_4$	140				
Physical treatment	Battery paste	500				
of batteries	Polypropylene	70 - 80				
	Residual plastics	100 - 130				
Smalting	Slag	150 - 200				
Smelting	Flue dust	25 - 60				
Refining	Dross	60 - 90				
Wastewater	Precipitated sludge					
Battery process- Blast						
Feed preparation	Spent acid	100				
	FePb Matte	< 150				
Shaft furnace	Slag	500				
	Flue dust	< 50				
Refining	Dross	80				
Primary lead shaft fur	ıace					
Sinter machine	Flue dust	Up to 100				
Sinter machine	Return sinter	Up to 3,000				
	$H_2SO_4$	600				
H <sub>2</sub> SO <sub>4</sub> plant	Calomel					
	Acid sludge					
Cd plant	CdZn precipitate					
Shaft furnace	Slag	500 + 600 return				
Shart furnace	Flue dust	Up to 80				
Wastewater treatment	Sludge	3				

Table 9. 9: Residues from secondary lead processes [78]

• Waste generation factors for copper thermal metallurgy: Waste generation factors for copper thermal metallurgy are given in Table 9. 10. Among these wastes only dust is regarded as hazardous wastes.

Process unit	By-product residue	Capacity (t/a)	Annual amount (t/a)	Waste generation factor (t/t)
Primary plant				
Flash smelting	Dust	220,000	100,000	0.45
furnace	Slag	220,000	400,000	1.81
Electric furnace	Dust	220,000	400	0.002
	Slag	220,000	400,000	1.81
Copper converter	Dust	220,000	4,000	0.02
Copper converter	Slag	220,000	150,000	0.68
Anode furnace	Dust	220,000	200	0.001
Anoue furnace	Slag	220,000	20,000	0.09
Sulfuric acid plant	Sulfuric acid	220,000	656,000	$2.98$ $^{*}$
Secondary plant				
Electric furnace	Dust	150,000	10,000	0.06
Electric furnace	Slag	150,000	40,000	0.26
Convertor	Dust	150,000	400	0.002
Converter	Slag	150,000	10,000	0.06
Continualt magaza	Dust	150,000	1,000	0.006
Contimelt process	Slag	150,000	2,000	0.012
Scrap converter	Dust	150,000	1,000	0.006
/TLA plant	Slag	150,000	2,000	0.012
Others				
Flaatrolysis	Anode slime	150,000	3,000	0.02
Electrolysis	Final liquor	150,000	$35,000 \text{ m}^2$	$0.23 \text{ m}^2/\text{t}$
Process wastewater treatment plant	Sludge	150,000	1,500	0.01
General	Household refuse	150,000	400	0.002

 Table 9. 10: Waste generation factors for copper thermal metallurgy

<sup>\*</sup> sold as a by-product

# 9.6 Hazardous Waste Generation from Thermal Processes

 Hazardous waste generation from power plants: Waste generation factor for FGD wastes is calculated. Capacity of each power station that has FGD system and sulfur content of coal or lignite is known. From these data FGD wastes, fly ash and bottom ash originating from power stations are calculated. Results are given in Table 9. 13.

• **Hazardous waste generation from aluminum thermal metallurgy:** Waste generation from primary aluminum production in Turkey is calculated using aluminum production data given for Turkey and waste generation factors tabulated in Table 9. 7. Results are tabulated in Table 9. 11. Among these wastes SPL do not fall into wastes from thermal processes (10). However, due to its refractory material content, it falls in to the category of *16 11 03*.

Source	Waste generation factor (kg per t of Al)	Quantity (t/yr)
Al skimmings	15 – 25	920 - 1,530
SPL	20 - 30	1,230 - 1,840
Other hazardous wastes	7 – 15	430 - 920
Non hazardous wastes	12 - 14	735 - 860
TOTAL (hazardous)		2,580 - 4,300

Table 9. 11: Specific waste quantities from primary aluminum production in Turkey

In Table 9. 12, waste generation from secondary aluminum production calculated for secondary aluminum production in Turkey is given.

 Table 9. 12: Approximate waste generation from secondary aluminum production

Residue	Waste generation factor (kg/t of Al produced)	Quantity (t/yr)	
Salt slag	Up to 500 kg/t Al	7,425	
	Up to 35 kg/t Al	520	
Filter dust	(0.1 – 1.0 kg/t Al –using Closed	(1.485 – 14.850 tons for Closed	
	Well furnace)	Well furnace)	
Furnace lining	~2 kg/t Al	30	
	~25 kg/t Al	370	
Skimmings	(40 – 80 kg/t Al –using Closed	(594 – 1 188 tons for Closed	
	Well furnace)	Well furnace)	
Dust	300 – 700 kg/t	4,455 - 10,400	
TOTAL		12,800 - 18,750	

Power Plant	Location	Capacity	Sulfur Content (%)	Gypsum amount (t/yr)	Bottom ash (t/yr)	Fly ash (t/yr)
Courbon	Ankara	2 x150MW	3.86	121,700	36	190,000
Çayırhan	Апкага	2 x160MW	3.80	130,000	37	200,000
Orhaneli	Bursa	1 x210MW	1.64	36,200	11	56,300
Afşin-Elbistan	K.Maraş	4 x360MW	2.0	303,000	90	471,000
Kemerköy	Muğla	3 x210MW	1.33	88,000	26	137,000
Yatağan	Muğla	3 x210MW	2.57	170,200	50.5	264,800
Kangal	Sivas	1 x157MW	3.2	53,000	15.5	82,150
İsken	İskenderun	1,320 MW	0.6-0.8	97,100	29	151,100
TOTAL				999,200	300	1,552,350

Table 9. 13: Amounts of FGD-Gypsum from power plants in Turkey

Therefore, total hazardous waste quantity produced as a result of primary and secondary aluminum production in Turkey is in the range of 15,350 – 23,180 tons/year.

Hazardous waste generation from lead thermal metallurgy: Average particulate lead emissions in Europe are in the range of 15 – 33 gr per ton of metal processed [78]. In Turkey 8,840 tons of lead scrap is processed to produce lead. Therefore, the amount of particulate lead emissions in Turkey is in the range of 132.6 – 291.72 kg/yr. this is an insignificant amount when compared to other wastes produced from lead thermal metallurgy.

Based on Table 9. 9 average values are calculated regarding emission factors of different process residues. These average values and the amount of generation in Turkey are given in Table 9. 14.

Wastes type	Average (kg/t of Pb)	Secondary lead production (tons/yr)	Waste produced in Turkey (tons/yr)
Slag	462.5 - 475	8,840	4,100 - 4,200
Flue dust	6.25 - 72.5	8,840	55 - 640
Dross	70 - 85	8,840	620 - 750
TOTAL			4,775 – 5,600

Table 9. 14: Average emission factors for process residues

As a result of these calculations, it can be concluded that total amount of hazardous wastes generated in Turkey as a result of lead product varies within the range of 4,775 - 5,600 tons/yr.

• **Hazardous waste generation from copper thermal metallurgy:** Wastes generated from thermal metallurgy are summarized in Table 9. 15. In order to determine the amount of hazardous wastes produced from copper thermal metallurgy, types of process units used in Karadeniz Bakır İşletmeleri A.Ş. is determined. Calculations were done according to flow diagram of Samsun facility of Karadeniz Bakır İşletmeleri A.Ş. Final liquor amount could not be estimated due to lack of data for electrolytic processes.

Although for thermal metallurgical processes of other metals slags are considered as hazardous wastes, for copper they are not classified as hazardous. As a consequence they are not considered in calculation for total hazardous wastes. This is also the case for electrolytic copper production wastes. In calculation only dust generated from pyrometallurgical processes of copper is taken into account.

Process unit	By-product residue	Waste generation factor (t/t)	Waste generated (t/yr)
Blister copper p	roduction		
Flash smelting	Dust	0.45	14,400
furnace	Slag	1.81	57,900
Copper	Dust	0.02	640
converter	Slag	0.68	21,760
Anode furnace	Dust	0.001	32
Anode Iumace	Slag	0.09	2,880
Electrolytic cop	per production		
Anode furnace	Dust	0.001	175
Anoue fuffiace	Slag	0.09	15,650
Flootrolygig	Anode slime	0.02	3,500
Electrolysis	Final liquor	$0.23 \text{ m}^2/\text{t}$	
TOTAL (hazar	dous)		15,250

Table 9. 15: Wastes generated from copper thermal metallurgy

Although for thermal metallurgical processes of other metals slags are considered as hazardous wastes, for copper they are not classified as hazardous. As a consequence they are not considered in calculation for total hazardous wastes. This is also the case for electrolytic copper production wastes. In calculation only dust generated from pyrometallurgical processes of copper is taken into account.

As a summary amounts of hazardous waste entries calculated for *Wastes from Thermal Processes (10)* is given in Table 9. 16.

Waste entry	Waste Generation (t/yr)
Wastes from aluminum thermal metallurgy (10 03)	
Al skimmings (10 03 15) *	920 - 1,530
SPL (16 11 03)	1,230 - 1,840
Other hazardous wastes	430 - 920
Salt slag from secondary production (10 03 08)	7,425
Filter dust (10 03 21) *	520
Furnace lining (16 11 03)	30
Skimmings (10 03 15) *	370
Dust (10 13 19) *	4,455 - 10,400
TOTAL	15,380 - 23,000

 Table 9. 16: Amounts hazardous waste entries calculated for 10

#### Table 9. 16 continued

Wastes from lead thermal metallurgy (10 04)	
Slag (10 04 01)	4,100 - 4,200
<i>Flue dust (10 04 04)</i>	55 - 640
Dross (10 04 02)	620 - 750
TOTAL	4,775 - 5,600
Wastes from copper thermal metallurgy (10 04)	
Dust (10 06 03)	15,250
TOTAL	15,250
Wastes from power stations and other combustion plants	(10 01)
<i>Wastes from gas cleaning containing dangerous substances (10 01 18)</i> <sup>*</sup>	999,200
Total for Wastes from Thermal Processes (10)	1,034,600 - 1,043,000
Minor entry	

Results obtained for wastes from thermal processes (10) are summarized in Table 9. 17.

#### 9.7 Comments

Although waste generation factors for zinc is available in the literature for both primary and secondary production no calculation could be done regarding zinc thermal metallurgy since there are no zinc producers in Turkey currently. The only pyrometallurgical zinc producer which was ÇİNKUR is closed. Moreover, zinc is not produced hydrometallurgically in Turkey.

For calculation of gypsum that is categorized as a minor entry in *wastes from power stations and other combustion plants (10 01)*, an example calculation was used given in Draft Reference Document on Best Available Techniques for Large Combustion Plants [79]. However, according to TEİAŞ based on the analysis made on these wastes, none of them proved to be hazardous. The reason for presenting this calculation in this thesis is that depending on the fuel used in power stations characteristics of gypsum changes. Therefore, in future gypsum generated from power station may be classified as hazardous wastes and the calculations given in this thesis represent the potential of hazardous wastes produced from power stations.

	Name of the e	Name of the entry         Amount generation		nt generated	ted (t/yr)	
2-digit	4-digit	6-digit	6-digit	4 digit	2 digit	
	Wastes from power stations	Oil fly ash and boiler dust (10 01 04)Sulfuric acid (10 01 09)Fly ash from emulsified hydrocarbonsused as fuel (10 01 13)Bottom ash, slag and boiler dust fromco-incineration containing dangeroussubstances (10 01 14)Fly ash from co-incinerationcontaining dangerous substances (10	  	-		
Wastes from Thermal Processes(10)	and other combustion plants (10 01)	Containing dangerous substances (1001 16)Wastes from gas cleaning containing dangerous substances (10 01 18)Sludges from on-site effluent treatment containing dangerous substances (10 01 20)Aqueous sludges from boiler	999,200 999,200 		1,034,600  1,043,000,	
		cleansing containing dangerous substances (10 01 22) Solid wastes from gas treatment containing dangerous substances (10				
	Wastes from the iron and steel industry (10 02)	02 07) Wastes from cooling water treatment containing oil (10 02 11)				
		Sludges and filter cakes from gas treatment containing dangerous substances (10 02 13)				

# Table 9. 17: Results obtained for wastes from thermal processes (10)

	Name of the entry		Name of the entryAmount generated (t/yr)			
2-digit	4-digit	6-digit	6-digit	4 digit	2 digit	
Wastes from Thermal	2-digit 4-digit			-	2 digit 1,034,600 -	
Processes(10)		Other particulates and dust (including ball-mill dust) containing dangerous substances (10 03 21)	520		1,043,000	
		Solid wastes from gas treatment containing dangerous substances (10 03 23)				
		Sludges and filter cakes from gas treatment containing dangerous substances (10 03 25)				
		Wastes from cooling-water treatment containing oil (10 03 27)				

# Table 9. 17 continued

	Name of the e	entry	Amount gen		
2-digit	4-digit	6-digit	6-digit	4 digit	2 digit
	Wastes from aluminum thermal metallurgy (10 03)	Wastes from treatment of salt slags and black drosses containing dangerous substances (10 03 29)			
		Slags from primary and secondary production (10 04 01) Dross and skimmings from primary and secondary production (10 04 02)	4,100 – 4,200 620 – 750		
		Calcium arsenate (10 04 03)			
	Wastes from lead thermal	Flue-gas dust (10 04 04)	55 - 640	4,775 –	1,034,600 
	metallurgy (10 04)	Other particulates and dust (10 04 05)		5,600	
		Solid wastes from gas treatment (10 04 06)		- ,	
Wastes from Thermal		sludges and filter cakes from gas treatment (10 04 07)			
Processes(10)		Wastes from cooling-water treatment containing oil (10 04 09)			
		<i>Flue-gas dust (10 05 03)</i>			
		Solid waste from gas treatment (10 05 05)			
	Waster from the ownal	Sludges and filter cakes from gas treatment (10 05 06)		-	
	Wastes from zinc thermal metallurgy (10 05)	Wastes from cooling-water treatment containing oil (10 05 08)			
		Dross and skimmings that are flammable or emit, upon contact with water, flammable gases in dangerous quantities (10 05 10)			

# Table 9. 17 continued

	Name of the	entry	Amou	nt genera	ted (t/yr)
2-digit	4-digit	6-digit	6-digit	4 digit	2 digit
		Flue-gas dust (10 06 01)	15,250		
		Solid waste from gas treatment (10 06 06)			
Wastes from copper metallurgy (10 06)	Wastes from copper thermal metallurgy (10 06)	Sludges and filter cakes from gas treatment (10 06 07)		15,250	
		Wastes from cooling-water treatment containing oil (10 06 09)			
	Wastes from silver, gold, platinum thermal metallurgy (1007)	<i>Wastes from cooling-water treatment containing oil (10 07 07)</i>			
		Salt slag from primary and secondary production (10 08 08)			1,034,60
	Wastes from other non-ferrous thermal metallurgy (10 08)	Dross and skimmings that are flammable or emit, upon contact with water, flammable gases in dangerous quantities (10 08 10)			1,043,00
		Tar-containing wastes from anode manufacture (10 08 12)			
		Flue-gas dust containing dangerous substances (10 08 15)			
		Sludges and filter cakes from flue-gas treatment containing dangerous substances (10 08 17)			
		<i>Wastes from cooling-water treatment containing oil (10 08 18)</i>			

Table 9. 17 continued

	Name of t	the entry	Amount generated (t/yr)		
2-digit	4-digit	6-digit	6-digit	4 digit	2 digit
		Casting cores and moulds which have not undergone pouring containing dangerous substances (10 09 05)			
		Casting cores and moulds which have undergone pouring containing dangerous substances (10 09 07)			
Wastes from Thermal Processes(10)	Wastes from casting of ferrous pieces (10 09)	Flue-gas dust containing dangerous substances (10 09 09)			
		Other particulates containing dangerous substances (10 09 11)			1,034,600
		Waste binders containing dangerous			
		Waste crack-indicating agent containing dangerous substances (10 09 15)			1,043,000
		Casting cores and moulds which have not undergone pouring, containing dangerous substances (10 10 05)			
	Wastes from casting of non- ferrous pieces (10 09)	Casting cores and moulds which have undergone pouring containing dangerous substances (10 10 07)			
		Flue-gas dust containing dangerous substances (10 09 09)			
		Other particulates containing dangerous substances (10 10 11)			

#### Table 9. 17 continued

	Name of the entry		Amount generated (t/yr)		
2-digit	4-digit	6-digit		4 digit	2 digit
	Wastes from casting of non-	Waste binders containing dangerous substances (10 10 13)			
	ferrous pieces (10 09)	<i>Waste crack-indicating agent containing dangerous substances (10 10 15)</i>			
		Waste preparation mixture before thermal processing, containing dangerous substances (10 11 09)			
		Waste glass in small particles and glass powder containing heavy metals (for example from cathode ray tubes) (10 11 11)			1,034,600
Wastes from Thermal	Wastes from manufacture of glass and glass products (10 11)	Glass-polishing and -grinding sludge containing dangerous substances (10 11 13)			
Processes(10)		Solid wastes from flue-gas treatment containing dangerous substances (10 11 15)			1,043,000
		Sludges and filter cakes from flue-gas treatment containing dangerous substances (10 11 17)			
		Solid wastes from on-site effluent treatment containing dangerous substances (10 11 19)			
	Wastes from manufacture of ceramic goods, bricks, tiles	Solid wastes from gas treatment containing dangerous substances (10 12 09)			
	<i>and construction products</i> (10 12)	Wastes from glazing containing heavy metals (10 12 11)			

Table 9. 17 continued

Table 7. 17 Commute	Table	9.	17	continued
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	Amoun	t generate	ed (t/yr)		
2-digit	4-digit	4-digit 6-digit			
Wastes from manufactu cement, lime and plaste		Wastes from asbestos-cement manufacture containing asbestos (10 13 09)			
Wastes from Thermal Processes(10)	and articles and products made from them (10 13)	Solid wastes from gas treatment containing dangerous substances (10 13 12)			1,034,600 - 1,043,000
	Waste from crematoria (10 14)	Waste from gas cleaning containing mercury (10 14 01)			

# **CHAPTER 10**

# WASTES FROM CHEMICAL SURFACE TREATMENT AND COATING OF METALS AND OTHER MATERIALS, NON-FERROUS HYDROMETALLURGY

#### 10.1 Objective and Scope

Objective of this chapter is to determine the amount of hazardous wastes generated from chemical surface treatment and coating of metals and other materials and from non-ferrous hydrometallurgy. According to EWC and Annex 7 of RCHW of Turkey this heading covers chemical surface treatment and coating of metals and other materials, non-ferrous hydrometallurgical processes, tempering processes and hot galvanizing processes [3,19].

#### 10.2 Introduction

Coating of metals, plastics and other materials covers a wide range of processes such as galvanic processes, zinc coating processes, pickling processes, etching, phosphatising, alkaline degreasing and anodizing. Some of these processes such as pickling aims to prepare the workpieces for subsequent coating processes.

Besides the variety of processes contained in the scope of coating, the types of materials coated and used for coating is highly variable.

 Hazardous Wastes Generated as a Result of Coating Processes and Non-ferrous Thermal Metallurgy

Wastes from chemical surface treatment and coating of metals and other materials and non-ferrous hydrometallurgy (11) are given in Appendix B. Absolute entries include pickling acids (11 01 05), acids not otherwise specified (11 01 06),

pickling bases (11 01 07), phosphatising sludges (11 01 08), saturated and spent ion exchange resins (11 01 16) under wastes from chemical surface treatment and coating of metals and other materials (11 01). Besides the absolute entries minor entries under wastes from chemical surface treatment and coating of metals and other materials(11 01) are sludges and filter cakes containing dangerous substances (11 01 09), aqueous rinsing liquids containing dangerous substances (11 01 11), degreasing waste containing dangerous substances (11 01 13), eluate and sludges from membrane systems or ion exchange systems containing dangerous substances (11 01 15) other wastes containing dangerous substances (11 01 98). Moreover, sludges from zinc hydrometallurgy (including jerosite and goethite) (11 02 02) are among absolute entries which not be covered in this thesis since no zinc is produced through hydrometallurgical route. Other 4-digit entries under 11 are sludges and solids from tempering process (11 03) and wastes from hot galvanizing processes (11 05). Absolute entries include wastes containing cyanide (11 03 01) and other wastes (11 03 02) under sludges and solids from tempering processes (11 03) and solid wastes from gas treatment (11 05 03) and spent flux (11 05 04) under wastes from hot galvanizing (11 05) [3,19].

10.4 Information Required for Determining Hazardous Wastes Generated from Coating Processes and Non-ferrous Hydrometallurgy

Information required for determination of hazardous waste generation from organic chemical processes can be listed as follows:

- 1 Waste from chemical surface treatment and coating of metals and other materials (11 01):
  - 1.1 **Types of chemical surface treatment processes applied in Turkey:** Major types of metal coating processes applied in Turkey are zinc coating, anodizing, silver/gold coating, chromium coating and nickel coating. Beside from theses, anodizing facilities are present.
  - 1.2 Total capacities of facilities applying each type of chemical surface treatment facilities: According to the Union of Chambers and

Commodity of Exchanges (TOBB) Industry Database<sup>†</sup> total capacity for coating processes in Turkey is given as:

- o 571,645 tons/yr
- 43,678,826 m<sup>2</sup>/yr and
- o 2,473,723 work pieces/yr [34].

This entry includes zinc, chromium, cadmium and nickel coating industry. There exist 233 facilities of this kind [34]. Finally, the capacity of anodizing in Turkey is 3,064 tons/yr that is 16,907,446 m<sup>2</sup> with 26 facilities [34]. According to the inquiry made in the database Table 10. 1 was prepared.

However, units of the given data is not clear in the sense that distinction cannot be made whether the units are based on the amount of material that is coated or amount of the material being used for coating of this reason it is assumed that capacity will be taken in terms of  $m^2$  of coated material and tons of work piece that is coated.

Moreover, although the number of facilities that apply different coating processes are given in the database, capacity data is not given for separate coating types and coating material used. For this reason, capacities for different coating processes are calculated assuming the capacity of each coating process is proportional to the number of facilities in operation.

Some facilities are classified in the "general" category in Table 10. 1 because of the fact that for some facilities the type of metal coating process is not specified in TOBB database [34]. In Table 10. 1 it is observed that percentage values found excluding the general category gives a better understanding of metal coating industry profile. Therefore, these values are used in further calculations. Moreover, although anodizing is given under a different category in Industry Database, there exists information regarding anodizing under Coating category. During calculation of capacity anodizing in Turkey these two values are added. Based on findings given in Table 10. 1, capacities of different metal coating processes are given in Table 10. 2.

<sup>&</sup>lt;sup>†</sup> TOBB Industry Database contains 66 000 entries throughout Turkey.

Province	General	Zinc coating	Anodizing	Silver/Gold coating	Nickel coating	Cadmiu m coating	Chromium coating	Combined
Adana	2	3						
Ankara	5	10	1	1				4
Bilecik							1	
Bolu	1				1			
Bursa	5	10			1		6	
Çorum	1							
Denizli							1	
Eskişehir		1			1			
Gaziantep	1							
İskenderun (Hatay)		1						
İstanbul	40	11	4	2	9		15	2
İzmir	9	5	1				2	
İzmit (Kocaeli)	2	6	1				5	1
Konya	3	5					3	
Malatya		1						
Manisa		1					2	
Nevşehir		1						
Sakarya	1	1						
Tekirdağ		1						
Kırıkkale		1						
Osmaniye		1						
TOTAL	70	59	7	3	12		35	7
PERCENT (including general category)	36,3	30,5	3,6	1,5	6,2		18,1	3,63
PERCENT (excluding general and combined category)		50,9	6,0	2,6	10,3		30,2	

# Table 10. 1: Metal coating industry profile in Turkey [34]

Process	Capacity		
	t/yr	$m^2$	work pieces
Zinc coating	290,967	22,188,845	1,256,651
Anodizing	37,362	2,620,730	148,423
Silver/Gold coating	14,863	1,135,650	64,317
Nickel coating	58,880	4,498,920	254,793
Chromium coating	172,636	13,191,000	747,065

Table 10. 2: Capacities of different metal coating processes in Turkey

No data could be found on Industry Database on phosphatising since rather no facilities reported on this category or facilities reported on this category are less than three.

1.3 Hazardous waste generation factors regarding chemical treatment of metals: Hazardous waste generation factors need to be identified for each type of coating processes, i.e. for each type of metal coated onto different types of substances. Moreover, hazardous waste generation factors for common surface treatment processes such as pickling and degreasing are required. Discussion about waste generation factors is given in Section 10.5.

#### 2 Wastes from non-ferrous hydrometallurgical processes (11 02):

- 2.1 **Types of non-ferrous minerals that are hydrometallurgically processed:** The only type of non-ferrous metal that was hydrometallurgically processed in Turkey was zinc.
- 2.2 **Capacities of facilities applying non-ferrous hydrometallurgical processes:** ÇİNKUR was the only facility hydrometallurgically processing zinc. However, this facility was recently closed. For this reason, no calculation could be made for *11 02*.
- 2.3 Waste generation factors for hydrometallurgical processes

#### **3** Sludges and solids from tempering processes (11 03):

3.1 **Types of materials for which tempering processes are applied**: No data could be obtained fro tempering processes in Turkey. As a result, no further determination could be made regarding *sludges and solids from tempering processes (11 03)*.

- 3.2 Capacities of facilities applying tempering processes
- 3.3 Waste generation factors regarding tempering processes
- **4** Wastes from hot galvanizing processes:
  - 4.1 Total capacities of facilities applying hot galvanizing: No information could be obtained on the extent of hot galvanizing processes in Turkey. Consequently, no further determination could be made on *wastes from hot galvanizing processes (11 05)*.
  - 4.2 Waste generation factors regarding hot galvanizing
- 10.5 Hazardous Waste Generation Factors for Coating Processes and Non-ferrous Hydrometallurgy

Waste generation from coating processes are highly variable due to different types of coating processes utilizing different types of metals. Moreover, coating industry comprises small scale facilities whose waste generation depends highly on plant management. These facts make it difficult to develop waste generation factors for metal coating industry However, degreasing and cleaning of workpieces is common in all metal coating processes. Table 10. 3 shows large differences which are found in practice [81].

Enterprise	Throughput of treated surface (m <sup>2</sup> /yr)	Consumption of cleaning agent (t/yr)	Specific consumption (t/100,000m <sup>2</sup> )
1	158,000	1.24	0.78
2	200,000	12.8	6.4
3	63,000	0.13	0.2
4	468,000	12.4	2.6
5	66,000	7	9.0

Table 10. 3: Examples of specific consumption rates in different plants [81]

There also are wide differences in the data for specific consumption of acids in pickling that is given in

Table 10. 4.

Enterprise	Throughput of coated surface (m²/yr)	Acid consumption (type and strength of acid not known) (t/yr)	Acid consumption (t/100,000m <sup>2</sup> )
1	158,000	24.0	15
2	200,000	202.0	101
3	63,000	21.0	33
4	468,000	150.0	32
5	60,000	1.3	2

Table 10. 4: Examples of acid consumption rates in different plants [81]

Although large differences exist as it is mentioned, average values and a range can be found for consumption of cleaning agents and pickling acid. These figures belong to consumption however; it can be assumed that all the cleaning agents and pickling acids consumed will be wasted whether or not they are recycled. According to this reasoning, waste factor for cleaning agents is in the range between 0.2 - 9.0 t / 100,000 m<sup>2</sup> and average quantity of cleaning agents wasted is 3.8 t / 100,000 m<sup>2</sup>. Waste factor for pickling acids is in the range of 2 - 101 t / 100,000 m<sup>2</sup>. Average quantity of pickling acids wasted is 3.6 t / 100,000 m<sup>2</sup>. Since both cleaning and pickling is applied for all metallic surface before coating, these waste factors will be used for all metal coating types.

As mentioned in previous section some metal is lost throughout the coating process. Metal losses from coating processes are given in Table 10. 5.

Process	Emission ratio (%)
Nickel (electrolytic)	19
Nickel (autocatalytic/chemical)	45
Nickel (phosphating)	55
Copper (electrolytic)	9
Copper (autocatalytic/chemical)	16
Zinc hot dip coating	6
Zinc (phosphating)	32
Cadmium (plating)	8
Chromium (hard)	40
Chromium (decorative)	52

Table 10. 5: Metal losses from coating process [81]

There are similar differences for the specific electrolyte consumption with zinc electroplating as given in Table 10. 6.

Enterprise	Throughput of coated surface (m²/yr)	Electrolyte consumption (t/yr)	Specific electrolyte consumption (t/100,000m <sup>2</sup> )
1	158,000	38.0	24
2	200,000	160.0	80
3	63,000	6.0	9.5
4	468,000	90.0	19.2
5	60,000	15.3	23

 Table 10. 6: Examples of electrolyte consumption rates in different plants [81]

As it is in the case of cleaning agents and pickling acids, these figures belong to consumption however; it can be assumed that all zinc electrolyte consumed will be wasted whether or not they are recycled. As a consequence, the range of zinc electrolyte usage is  $9.5 - 80 \text{ t} / 100,000 \text{ m}^2$  with an average of  $31.1 \text{ t} / 100,000 \text{ m}^2$ .

Raw wastewater production from electroplating industry calculated from quantity of anode used is given in Table 10. 7. Figures given in this table can only be used for calculations when information about the amount of coating material rather than coated material is known.

Metal	Wastewater (m <sup>3</sup> /t of metal deposited)	Wastewater (kg/t of metal deposited)
Copper (Cu)	1,403	9.77 Cu + 20 CN *
Nickel (Ni)	1,519	3.98 Ni
Chromate (Cr <sub>2</sub> O <sub>3</sub> )	36,300	743 Cr (total) and 297 Cr <sup>+6</sup>
Zinc (Zn)	1,815	224 Zn + 32.5 CN
Cadmium (Cd)	883	Unknown amount of Cd + 12.7 CN
Tin (Sn)	1,125	Unknown amount of Sn

 Table 10. 7: Raw waste calculation from quantity of anode used [82]

<sup>\*</sup> If cyanide bath is used

Moreover, raw waste calculations based on amperes of electricity consumed per hour or on electrodeposited area produced is given in Table 10. 8.

Metal bath	Waste volume (m <sup>3</sup> /ampere/h)	Dry waste (mg/ampere/h)	Waste volume (m <sup>3</sup> /m <sup>2</sup> )	Dry waste (mg/m <sup>2</sup> )
Copper bath	1.67	11.6	94	658
Nickel bath	1.66	4.35	103	270
Chrome bath	1.66	13.6 Cr <sup>+6</sup> + 34 Cr (total)	95	918 Cr <sup>+6</sup> , 1946 Cr (total)
Zinc bath	1.52	205	93	12 448
Cyanide bath of any kind		23.8		1,333

 Table 10. 8: Raw waste calculations based on amperes of electricity consumed per hour or on electrodeposited area [82]

# 10.6 Hazardous Waste Generation from Metal Coating Industry in Turkey

In Table 10. 9 the amount of wastes originating from chemical surface treatment and coating industry in Turkey is summarized.

Table 10. 9: Quantity of wastes originating from chemical surface treatment and coating of metals

Type of waste	Waste generation factor	Capacity	Quantity of waste (t/yr)
Cleaning	$0.2 - 9.0 \text{ t} / 100,000 \text{ m}^2/\text{yr}$	$606 \text{ x } 10^5 \text{ m}^2$	120 - 5,450
agents	3.8 t / 100,000 m <sup>2</sup> /yr	$606 \text{ x } 10^5 \text{ m}^2$	2,300
Pickling	$2 - 101 \text{ t} / 100,000 \text{ m}^2/\text{yr}$	$606 \text{ x } 10^5 \text{ m}^2$	1,210 - 61,200
acids	36.6 t / 100,000 m <sup>2</sup> /yr	$606 \text{ x } 10^5 \text{ m}^2$	22,180
TOTAL			1,330 - 66,650

## 10.7 Comments

Although waste generation factors are found for cleaning agents, acids, metal losses from coating process, electrolyte consumption, wastewater, solid waste no calculation could be done due to lack of capacity data. For determination of wastes from chemical surface treatment and coating of metals and other materials (11 01) capacity information taken from TOBB industrial database was used. However, capacity values were given as a total in the database i.e. capacities for different coating processes are not given. Estimation is made for separate processes based on number of facilities applying different coating processes. Moreover, there is confusion over units of capacities. From the units given along with the capacities it is not possible to distinguish whether the capacity represent amount of metal coated or amount of metal being coated onto another material. Unfortunately, the staffs of TOBB are not sure what the units stand for. The capacities obtained from Industry Database are not clear and detailed. Therefore, capacity estimation should be established for metal coating industry for Turkey.

	Name of the	entry	Amou	int generate	d (t/yr)
2-digit	4-digit	6-digit	6-digit	4 digit	2 digit
	Pickling acids (11 01 05)	1,210 – 61,200			
	Acids not otherwise specified (11 01 06)				
		Pickling bases (11 01 07)			
	Waster from chamical	Phosphatising sludges (11 01 08)			
Wastes from	Wastes from chemical surface treatment and coating of metals and other	Sludges and filter cakes containing dangerous substances (11 01 09)			
chemical surface	· · ·	Aqueous rinsing liquids containing dangerous substances (11 01 11)		- 1,330 - 66,650	1,330 – 66,650
coating of metals	galvanic processes, zinc coating processes, pickling	Degreasing wastes containing	1,210 –		
and other	processes, etching,	dangerous substances (11 01 13)	61,200		
materials and non-ferrous hydrometallurgy (11)	materials and non-ferrousphosphatising, alkaline degreasing, anodizing) (11 01)	Eluate and sludges from membrane systems or ion exchange systems containing dangerous substances (11 01 15)			
	Saturated or spent ion exchange resins (11 01 06)				
	<i>Other wastes containing dangerous</i> <i>substances (11 01 98)</i>				
	Wastes from non-ferrous hydrometallurgical processes (11 02)	Sludges from zinc hydrometallurgy (including jarosite, goethite) (11 02 02)			

 Table 10. 10: Results obtained for wastes from chemical surface treatment and coating of metals and other materials; non-ferrous hydrometallurgy (11)

Name of the entry			Amou	nt generated	(t/yr)
2-digit	4-digit	6-digit	6-digit	4 digit	2 digit
Wastes from chemical surface treatment and coating of metals and other		Wastes from copper hydrometallurgical processes containing dangerous substances (11 02 05)			
	processes (11 02)	<i>Other wastes containing dangerous</i> <i>substances (11 02 07)</i>			1,330 -
materials and	Sludges and solids from	Wastes containing cyanide (11 03 01)			66,650
non-ferrous tempering processes (11 03)	<i>Other wastes (11 03 02)</i>				
	Wastes from hot galvanizing processes (11 05)	Solid wastes from gas treatment (11 05 03)			
processes (11 05)		Spent flux (11 05 04)			

# Table 10. 10 continued

# **CHAPTER 11**

# **OIL WASTES AND WASTES OF LIQUID FUELS**

#### 11.1 Objective and Scope

Objective of this chapter is to determine the amount of waste oils generated throughout Turkey. According to EWC and Annex 7 of RCHW of Turkey the term waste oils include waste hydraulic oils, waste engine, gear and lubricating oils, waste insulating and heat transmission oils, bilge oils, oil/water separator contents, wastes of liquid fuels and oils wastes not otherwise specified [3,19].

# 11.2 Introduction

Oils refined from crude petroleum in refineries are used in nearly all of the vehicles as fuels and engine oils. Moreover, they are used in most of the hydraulic systems of cranes, elevators etc. In some equipment, oils are used for insulation to protect the equipment or for transmission of heat within the system. Another application of oils is for lubricating purposes thus for protecting the equipments from heat and friction created within the operation. In most cases waste fuels are not generated from vehicles. However, from transportation of fuels and pumping stations waste fuels can be generated. Hydraulic oils used in different equipments needs to be replaced from time to time. This holds also for engine oils. Lubricating oils are usually consumed only when the target equipment operates. Bilge oils are generated from ships and need to be collected periodically. Lastly, in various cases oil/water separators are employed in industry and wastewater treatment plants.

#### 11.3 Hazardous Wastes Generated from Use of Oils

According to EWC and Annex 7 of RCHW waste oils are listed under *oil wastes and wastes of liquid fuels (13)* and all types of waste oils mentioned in Section 11.1 are regarded as absolute entries. The complete list of wastes under *oil wastes and wastes of liquid fuels (13)* is given Appendix B.

#### 11.4 Information Required for Determining the Amount of Waste Oils

Information necessary to determine the amount of waste oils include capacity information (i.e. the types and amounts of oils utilizing vehicles and equipment) and waste generation factors. No waste generation factor could be found from the literature for either of waste oils. For this reason waste generation factor is developed for engine oils and direct information was tried to be obtained. Information necessary for determination of amount of waste oils and information available can be listed as follows:

#### 1 Waste hydraulic oils:

- 1.1 **Types of equipment utilizing hydraulic oils**: The highest amounts of hydraulic oils are used in elevators and construction vehicles such as cranes.
- 1.2 The number of equipment utilizing hydraulic oils: It was not possible to determine the number of construction vehicles utilizing hydraulic oils. For elevators information was requested from TASIAD (Tüm Asansör Sanayici ve İş Adamları Derneği) however, no results could be obtained [96].
- 1.3 The amount of hydraulic oils utilized in each type of equipment: Due to lack of information in equipment utilizing hydraulic oils further research could not be accomplished.
- 1.4 The amount of hydraulic oil lost during operation

#### 2 Waste engine, gear and lubricating oils

2.1 **Types of vehicles and equipment utilizing engine and lubricating oils:** Lubricating oils has wide range of applications in different equipments which could not be identified clearly. Other than lubricating oils all types of vehicles use engine oils.

2.2 **The number of vehicles equipment utilizing engine and lubricating oils**: The number of vehicles in Turkey is determined and given in Table 11. 1.

Type of vehicle	Number of vehicles
Automobiles	5 624 046
Minibus	330 064
Bus	158 331
Trucks and pickup trucks	2 051 037
Tractors	1 231 356

Table 11. 1: Number of vehicles in Turkey [83]

2.3 The amount of engine and lubricating oils in each type of vehicle and equipment: Another issue for lubricating oils arises when amount of lubricating oil is considered. As stated previously lubricating oils are used during the operation for protection of equipment. The amount used in the processes is highly variable. Since equipment utilizing lubricating oil could not be identified, the amount used for each equipment could not be identified either. Each type of vehicle has different storage capacities for engine oils. According to the direct information obtained from automobile, truck and tractor services average amounts of engine oils in different vehicles are as given in Table 11. 2.

Type of vehicle	Average mineral oil amount (L)
Automobiles	4 – 5
Minibus	5 – 7
Bus	16
Trucks and pickup trucks	10 - 15
Tractors	7 – 12

 Table 11. 2: Engine oil storage capacity of different vehicles

2.4 The amount of engine and lubricating oils lost in each type of vehicle and equipment during operation: Amount of engine oils lost in each type of vehicle is assumed by consulting vehicle services of different types of vehicles. The assumptions are given in Table 11. 3.

Type of vehicle	Average mineral oil lost per replacement of oils(L)
Automobiles	0.5 – 1
Minibus	0.5 – 1
Bus	0.5 – 1
Trucks and pickup trucks	0.5 – 1
Tractors	0.5 - 1

 Table 11. 3: The amount of engine oil lost per replacement of oils

- 2.5 **Engine oil replacement period**: It is assumed that engine oils are replaced in 10,000 km for each type of vehicle.
- 2.6 **Average amount of usage**: Different types of vehicles have different amounts of use in a year. Values given in Table 11. 4 is gathered by consulting vehicle services.

Table 11. 4: Average amount o	f usage of differen	t types of vehicles
-------------------------------	---------------------	---------------------

Type of vehicle	Average amount of usage (km/yr)
Automobiles	10,000 - 25,000
Minibus	60,000–75,000
Bus	275,000-350,000
Trucks and pickup trucks	100,000-150,000
Tractors	650–700h/yr

For engine oils the engine oil capacity and the amount of engine oil lost between the replacements are determined. Therefore, the amount of waste engine oils generated at each replacement can be found for each type of vehicle.

# 3 Waste insulating and heat transmission oils

- 3.1 Types of equipment utilizing insulating and heat transmission oils: Major type of equipment utilizing insulating oils is transformers used in electricity distribution.
- 3.2 **The number of equipment utilizing insulating and heat transmission oils**: According to the direct information obtained from TEİAŞ the number of transformers in Turkey is as given in Table 11. 5.

	440 kV	154 kV	66 kV or less	TOTAL
Number of transformers	116	893	63	1072
Capacity (MVA)	20 110.0	46 420.4	734.3	67 084.7

Table 11. 5: Number of transformers in Turkey [84]

Direct information obtained from TEİAŞ, for the amount of waste insulating oils generated in Turkey.

#### 4 **Bilge oils:**

- 4.1 **The number of vehicles generating bilge oils:** The discharge of bilge oil is closely related to the number of ships docking in ports. There are no constant values for number of ships docking to a given port.
- 4.2 **The amount of bilge oils generated from vehicles:** It is stated by İZAYDAŞ personnel reported that total amount of bilge oils incinerated is highly variable depending on the number of ships and age of ships.

Research done for bilge oils which did not give any results. According to Turkish Undersecretariat for Maritime Affairs, starting this year, all the ships using ports should report the amount of bilge oils that is to be disposed in Turkey. However, declaration forms for year 2005 have not reached the Turkish Undersecretariat for Maritime Affairs. The only disposal means for these kinds of oily wastes are incineration at İZAYDAŞ, İzmit. Moreover, it is quoted that İZAYDAŞ do not has a prediction for bilge oils that would arrive at İZAYDAŞ in future.

#### 5 Oil/water separator contents:

- 5.1 Industrial processes using oil/water separators within the process or for treatment purposes: The industrial processes using oil/water separators could not be identified. For this reason no further calculation could be done for determining the amount of oil/water separator contents.
- 5.2 The number of oil/water separators

# 5.3 Waste generation factor regarding the amount of oil/water separator content generated per oil/water separator

- 6 **Wastes of fuels**: As mentioned fuel wastes are likely to occur in spills during transportation of fuels or in pumping stations.
  - 6.1 Waste generation factor regarding the amount of fuel wastes in transportation or in each pumping station: No such waste generation factor could be found in literature. This is due to the fact that the amount of fuel wasted is highly dependent on the care taken in transportation and pumping stations. It is difficult to predict the amount of waste fuels by using a waste generation factor.
- 11.5 Waste Generation Factors for Oil Wastes and Wastes of Liquid Fuels

Waste generation factors determined for waste oils are listed as follows:

• Waste engine oils: Waste generation factor is determined from subtracting the amount of engine oil lost within a vehicle in a year from the total amount of engine oil found in the vehicle. Waste generation factors developed for waste engine oils are presented in Table 11. 6.

In order to develop these waste generation factors the number of replacements is multiplied by the amount of engine oil wasted. It is assumed that engine oils are replaced in each type of vehicle at every 10,000 km. By using the data given in Table 11. 4 the number of replacements are calculated. The capacity of vehicles to store engine oils and the amount of engine oil lost between engine oil replacements are assumed as given in Table 11. 2 and Table 11. 3. From these information Table 11. 6 summarizing waste generation factors is constructed.

Type of vehicle	Average mineral oil amount (L)	Mineral oil change (per yr)	Average mineral oil lost (L)	Waste generation factor (L/yr/vehicle)
Automobiles	5	1	0.75	4.25
Minibus	6	6	0.75	31.5
Bus	16	28	0.75	425
Truck and pickup truck	10	10	0.75	92.5
Tractor	11	3	0.75	31

Table 11. 6: Assumptions used in calculation of waste mineral oils

- Waste insulating and heat transmission oils: Direct information is obtained regarding the amount of waste insulating and heat transmission oils.
- 11.6 Hazardous Waste Generation from Waste Oils
  - Waste engine oils: By using the number of vehicles given in Table 11. 1 and waste generation factors developed in Table 11. 6 the amount of waste engine oils generated in Turkey are calculated. The results are given in Table 11. 7.

Type of vehicle	Number of vehicles	Amount of mineral oil wasted (m <sup>3</sup> /yr)
Automobiles	5,624,046	24,000
Minibus	330,064	10,300
Bus	158,331	67,300
Truck	2,051,037	190,000
Tractor	1,231,356	38,000
TOTAL	329,600	

Table 11. 7: Waste oil generated from vehicles

• Waste insulating and heat transmission oils: Direct information is obtained from TEİAŞ regarding the amount of waste transformer oils which can be categorized as insulating oils. According to TEİAŞ **1000 tons** of waste transformer oils are being generated each year. Considering the capacity information of transformers in Turkey, this means that each transformer generates 5.2 kg of waste oil/kV.

Findings regarding *oil wastes and wastes of liquid fuels* (13) are summarized in Table 11. 8.
Name of the entry Amount generated (t/yr) 2 digit 4 Digit 4 digit 2 digit Waste hydraulic oils (13 01) --291,000 Waste engine, gear, lubricating oils (13 02) Waste insulating and heat transmission oils (13 03) Oil Wastes and Wastes of 1000 291,000 Liquid Fuels (13) Bilge oils (13 04) --Oil/water separator contents (13 05) --Wastes of liquid fuels (13 07) \_\_\_

Table 11. 8: Findings regarding oil wastes and wastes of liquid fuels (13)

# WASTE ORGANIC SOLVENTS, REFRIGERANTS AND PROPELLANTS

#### 12.1 Objective and Scope

Objective of this chapter is to determine the amount of hazardous wastes generated from industries utilizing organic solvents, refrigerants and propellants.

#### 12.2 Introduction

Organic solvents are described as any Volatile Organic Compounds (VOC) which is used alone or in combination with other agents, and without undergoing a chemical change, to dissolve raw materials, products or waste materials, or is used as a cleaning agent to dissolve contaminants, or as a dissolver, or as a dispersion medium, or as a viscosity adjuster, or as a surface tension adjuster, or a plasticizer, or as a preservative [95]. Moreover, halogenated solvents are described as an organic solvent which contains at least one atom of bromine, chlorine, fluorine or iodine per molecule [85].

According to the COUNCIL DIRECTIVE 1999/13/EC the activities in which solvents are used are listed as follows:

- o Adhesive coating
- Coating activity in which a single or multiple application of a continuous film of coating is applied to vehicles (new cars, truck cabins, vans and trucks and busses etc.), trailers, metallic and plastic surfaces, wooden surfaces, textile, fabric, film and paper surfaces and leather.

- Coil coating where coiled steel, stainless steel, coated steel, copper alloys or aluminum strips is coated with either a film forming or laminate coating in a continuous process.
- Dry cleaning
- Footwear manufacture
- o Manufacturing of coating preparations, varnishes, inks and adhesives
- o Manufacture of pharmaceutical products
- Printing in which, with the use of an image carrier, ink is transferred onto whatever type of surface (flexography, heatset web offset, laminating associated to a printing activity, publication rotogravure, rotogravure, rotary screen printing, varnishing).
- Rubber conversion
- Surface cleaning
- o Vegetable oil and animal fat extraction and vegetable oil refining activities
- Vehicle refinishing
- Winding wire coating
- Wood impregnation
- Wood and plastic lamination [81]
- 12.3 Hazardous Wastes Generated as a Result of Organic Solvents, Refrigerants and Propellants Utilizing Processes

Hazardous wastes listed under *waste organic solvents, refrigerants and foam/aerosol propellants (14 06)* include *chloroflorocarbons (CFCs) (14 06 01), other halogenated solvent and solvent mixtures (14 06 02), other solvents and solvent mixtures (14 06 03), sludges or solid wastes containing halogenated solvents (14 06 04)* and *sludges or solid wastes containing other solvents (14 06 05)* [3,19].

12.4 Information Required for Determining Hazardous Wastes Generated from Organic Solvents, Refrigerants and Propellants

Information required for determination of hazardous waste generation from organic chemical processes can be listed as follows:

- 1 Types of processes in which organic solvents, refrigerants and propellants are used: Processes utilizing organic solvents are identified as given in Section 12.2. The list includes many different industries and processes. For this reason, two representative industries are chosen. First one is the dry cleaning industry and the second one is printing industry. Choice of these two industries is based on the number of facilities related to the sectors listed in Section 12.2 in Turkey. Dry cleaning industry contains highest number of facilities followed by printing industry. Consequently, it is assumed that when dry cleaning and printing industry is covered most of the wastes that fall under *waste organic solvents, refrigerants and propellants (14)* would be determined. Unfortunately, a list of industries and processes utilizing refrigerants and propellants could not be identified. As a result, wastes resulting from use of refrigerants and propellants could not be determined.
- 2 Capacities of dry cleaning facilities: Although the capacity of dry cleaners is not documented, according to one estimate there are 6000 dry cleaners in Turkey. Based on personal information obtained each dry cleaner processes 75 150 clothes in a single day. Assuming an average weight of 0.75 kg of each item processed, this yields to 56.25 112.5 kg of cloth processed per dry cleaner per day. General amount of clothes dry cleaned in Turkey is 123,200 246,400 ton of cloth per year [87].
- 3 Capacities of printing industry: According to data obtained from Union of Chambers and Commodity of Exchanges (TOBB) Industry Database Table 12. 1 is formed.

According to information obtained via personal communication weight of the newspaper changes within the range of  $48.8 - 52 \text{ g/m}^2$  with an average of 50 g/m<sup>2</sup>. This means that each year the amount of newspaper printed is 445,450 tons. Other than that information about the weight of books, magazines, brochure lacks. It is difficult to estimate the total weight of material printed as books, magazines, brochures etc. These items can be printed on glossy paper, first grade paper or second grade paper. It is assumed that the weight of these paper are around 60 g/m<sup>2</sup> which leads to total amount of 16,244 tons of paper printed as book, magazines and brochure.

Printing type	Printing process	Capacity
Newspaper	Offect lithegraphy or relief printing	650,029,464 pieces
printing	Offset lithography or relief printing	8,909,032,753 m <sup>2</sup>
Books,		5,559,721,890 pieces
magazines, brochure	Offset lithography or relief printing	270,729,319 m <sup>2</sup>
		1,443,524,728 pieces
Advertising	Digital or screen printing	412,609,726 kg
		$65,609,276 \text{ m}^2$
		3,166,230,640 pieces
Packaging	Gravure or relief printing	2,748,446 tons
		1,726,308,595 m <sup>2</sup>
Business	Offset lithography	6,735,642,459 pieces
stationary	Onset htnography	9,508 tons
Ant prints		1,189,274,992 pieces
Art prints, invitations etc.	Offset lithography or gravure	1,059,381,744 m <sup>2</sup>
invitations etc.		96,167,424 tons

Table 12. 1: Capacity of printing industry in Turkey [34]

In further calculations, books, brochures, magazines and business stationeries are assumed to be printed by using heatset offset. Newspapers assumed to be printed by letterpress and packaging materials assumed to be printed by gravure.

- 4 **Hazardous waste generation factors for dry cleaning industry**: Hazardous waste generation factors related to dry cleaning industry is given in Section 12.5.
- 5 Hazardous waste generation factors for printing industry: Hazardous waste generation factors related to printing industry is given in Section 12.5.
- 12.5 Hazardous Waste Generation Factors for Waste Organic Solvents, Refrigerants and Propellants
  - Hazardous waste generation factors for dry cleaning industry: Hazardous wastes in dry cleaning process are still residues, spent cartridge filters and cooked powder residues whose typical generation amounts are given in Table 12. 2.

Type of hazardous waste		Typical amount of hazardous waste (kg)
Still residues		25
Spent cartridge filters	Standard (carbon core)	20
	Adsorptive (split)	30
Cooked powder residues		40

 Table 12. 2: Typical amounts of hazardous wastes generated by a perc-dry cleaning facility (for every 1000 kg of clothes cleaned) [85]

• **Hazardous waste generation factors for printing industry**: Hazardous waste generation factors for printing industry are given in Table 12. 3.

Waste	Waste Generation Factor	Unit
Heatset offset		
Dampening	$1.11*10^{-4}$	t/t of commercial
solution residues	1.11*10	product
Mixture of cleaning	$1.27*10^{-3}$	t/t of commercial
agents and water	1.27 10	product
Cleaning wipes	5.55	Items/t of
Cleaning wipes	5.55	commercial product
VOC in waste	$1.11*10^{-4}$	t/t of commercial
	1.11 10	product
Letterpress and lett	erset	
Mixture of cleaning	$1.27*10^{-3}$	t/t of commercial
agents and water		product
Flexible package pr	inting, flexography, gr $4.22 * 10^{-3}$	avure
	$4.22 * 10^{-3}$	t/t of product
Mixture of cleaning	$1.54 * 10^{-3}$	t/t of product
agents and water		-
Process water	0.056	m <sup>3</sup> /t of product
Wipes	14.85	Items/t of product
VOC in waste	$2.37 * 10^{-3}$	t/yr
Publication gravure	;	
Substrate/misprints	0.092	t/ t of product
Ink/varnish	$1.81 * 10^{-4}$	t/ t of product
residues		-
Sludge	8.68 10 <sup>-5</sup>	t/ t of product
Activated carbon	3.01 10 <sup>-5</sup>	t/ t of product
VOC in waste	$2.31 \ 10^{-5}$	t/ t of product

 Table 12. 3: Hazardous waste generation factors for printing processes

- 12.6 Hazardous Waste Generation from Organic Solvent, Refrigerants and Propellants Utilizing Processes
  - **Hazardous waste generation from dry cleaning industry:** It was estimated that total amount of cloths processed in dry cleaners is 123,200 246,400 ton of cloth per year. Based on this figure, total hazardous waste generation from dry cleaning industry is calculated as given in Table 12. 4.

Table 12. 4: Typical amounts of hazardous wastes generated by a perc-dry cleaning facility<br/>(for entry 14 06 05) [85]

Type of hazardous waste		Typical amount of hazardous waste (kg)	Hazardous waste generation (t/yr)
Still residues		25	3,080 - 6,150
Spent cartridge filters	Standard (carbon core)	20	2,460 - 4,920
	Adsorptive (split)	30	3,700 - 7400
Cooked powder residues		40	5,000 - 10,000
TOTAL			14,240 - 28,470

• **Hazardous waste generation from printing industry**: Amount of hazardous wastes generated from printing industry in Turkey is given in Table 12. 5.

Waste	Waste Generation Factor	Wastes Generated	Entry
Heatset offset			
Dampening solution residues	1.11*10 <sup>-4</sup> t/t	3 t/yr	14 06 05
Mixture of cleaning agents and water	1.27*10 <sup>-3</sup> t/t	33 t/yr	14 06 05
Cleaning wipes	5.55 Items/t	141,636 Items/yr	14 06 05
VOC in waste	$1.11*10^{-4}$ t/t	3 t/yr	
Letterpress and letterset			
Mixture of cleaning agents and water	$1.27*10^{-3}$ t/t	565 t/yr	14 06 05
Flexible package printing	g, flexography, gravu	re	
Ink residues	$4.22 * 10^{-3} t/t$	11,600 t/yr	14 06 05
Mixture of cleaning agents and water	$1.54 * 10^{-3} t/t$	4,230 t/yr	14 06 05

Table 12. 5: Hazardous waste generation from printing industry in Turkey

Waste	Aste Waste Generation Factor Wastes Generated		Entry				
Flexible package pri	Flexible package printing, flexography, gravure						
Process water	$0.056 \text{ m}^3/\text{t}$	153,912m <sup>3</sup> /yr	14 06 02				
Wipes	14.85 Items/t	40,814,423 Items/yr	14 06 05				
VOC in waste	$2.37 * 10^{-3}$	6,515 t/yr					
Publication gravure							
Ink/varnish residues	1.81 * 10 <sup>-4</sup> t/ t	17,400t/yr	14 06 05				
Sludge	8.68 10 <sup>-5</sup> t/ t	8,350 t/yr	14 06 05				
Activated carbon	3.01 10 <sup>-5</sup> t/ t	2,900 t/yr	06 13 02				
VOC in waste	2.31 10 <sup>-5</sup> t/ t	2,220 t/yr					
TOTAL		53,820 t/y 41,000,000 items/yr 153,912m <sup>3</sup> /yr					

Table 12. 5 continued

Findings regarding *waste organic solvents, refrigerants and propellants (14)* are summarized in Table 11. 8.

## 12.7 Comments

Although in Council Directive 1999/13/EC industries that utilize solvent in their manufacturing processes are specified, two largest industries are covered in this thesis, that are dry cleaning and printing industry [95]. Capacity information related to the other industries proves to be difficult to gather. Moreover, waste generation factors for these industries are not readily available.

Name of the entry		Amour	nt generated	(t/yr)	
2-digit	4-digit	6-digit	6-digit	4 digit	2 digit
	Chlorofluorocarbons, HCFC, HFC (14 06 01)				
Waste Organic	Solvents, refrigerants and	Other halogenated solvents and solvent mixtures (14 06 02)		- 229,670 530 - 243,900	229,670 – 243,900
Solvents, Refrigerants and		Other solvents and solvent mixtures (14 06 03)	212,530		
Propellants (14)	06)	Sludges or solid wastes containing halogenated solvents (14 06 04)		243,900	
	Sludges or solid wastes containing	14,240 -			
		other solvents (14 06 05)	28,470		

 Table 12. 6: Results obtained for waste organic solvents, refrigerants and propellants (14)

## WASTES FROM ELECTRICAL AND ELECTRONIC EQUIPMENT

#### 13.1 Objective and Scope

Objective of this chapter is to present an example for determination of hazardous wastes listed under *wastes from electrical and electronic equipment (16 02)*. Printing circuit boards (PCB) manufacture is chosen as a representative industry.

13.2 Introduction

Electrical and electronic equipment are composed of many materials and parts. Considering the wide range of electrical and electronic equipment it is difficult to come up with general waste generation factors. Printed circuit boards (PCBs) are covered whose production processes are given in Appendix B as an example [3,19].

#### 13.3 Hazardous Wastes Generated as a Result of PCB Manufacture

Under the entry of 16 02 wastes from electrical and electronic equipment 6digit entries are 16 02 09 transformers and capacitors containing PCBs (minor entry), 16 02 10 discarded equipment containing or contaminated by PCBs other than those mentioned in 16 02 09 (minor entry), 16 02 11 discarded equipment containing chlorofluorocarbons, HCFC, HFC (minor entry), 16 02 12 discarded equipment containing free asbestos (minor entry), 16 02 13 discarded equipment containing hazardous components2 other than those mentioned in 16 02 09 to 16 02 12 (minor entry), 16 02 15\* hazardous components removed from discarded equipment (absolute entry)

## 13.3.1 Information Required for Determining Hazardous Wastes Generated from PCB Manufacture

Information required for determination of hazardous waste generation from organic chemical processes can be listed as follows:

1 Capacities of PCB manufacturing facilities: PCB production in Turkey is given Table 13. 1.

Producer	Capacity * (m <sup>2</sup> /yr)
Denge Elektronik Baskılı Devre Matbaacılık A.Ş.	60 000
Delron Elektronik Sanayii ve Ticaret A.Ş.	15 000
ASELSAN	12 000
Baskı Devre	2 000
Grafsan Elektronik Baskıdevre San. Ve Tic. Ltd. Şti.	750
TOTAL	89 750

Table 13. 1: PCB production capacity in Turkey

<sup>\*</sup> Information obtained from personal communication

**2** Waste generation factors related to PCB manufacture: Waste generation factors for PCB production processes are given in Section 13.5.

#### 13.4 Hazardous Waste Generation Factors for PCB Manufacture

Types of wastes that can be originating from PCB manufacture is given in Table 13. 2 along with waste generation factors. Note that waste types originating from PCB manufacture belong to different entries not only *16 02* [3].

Among these wastes 11 01 09 and 11 01 99 are classified as minor entries and 11 01 05 and 11 01 07 are listed as absolute entries. Unfortunately no waste factor could be developed for 16 02 [19]. However, at the end of their life span, discarded PCBs will contain the amounts of hazardous waste given in Table 13. 2.

PCB wastes arising	Indicative HWL Number	Maximum quantity (kg/1000 m <sup>2</sup> )
Sludges which may contain hazardous substances from physico- chemical treatment	11 01 09	2,500
Sludges from an in-house water treatment plant	11 01 09	1,000
Acidic pickling agents	11 01 05	3,000
Alkaline pickling agents	11 01 07	2,500
Drill entry boards		800
Precious metals/metals (Ag, Au, Cu, Ni, Pd, Sn, Pb)	11 01 99	<100 - 150

 Table 13. 2: Wastes arising from PCB manufacture [89]

## 13.5 Hazardous Waste Generation from PCB Manufacture in Turkey

PCB production is calculated by multiplying yearly manufacture of PCB with waste generation factors given in Table 13. 3. Waste production from PCB production is given in Table 13. 3.

PCB wastes arising	Entry	Maximum quantity (kg/1000 m <sup>2</sup> )	Capacity (m²/yr)	Waste produced (t/yr)
Sludges which may contain hazardous substances from physico-chemical treatment	11 01 09	2500	89,750	225
Sludges from an in-house water treatment plant	11 01 09	1000	89 750	90
Acidic pickling agents	11 01 05	3000	89 750	270
Alkaline pickling agents	11 01 07	2500	89 750	225
Drill entry boards		800	89 750	0.72
Precious metals/metals (Ag, Au, Cu, Ni, Pd, Sn, Pb)	11 01 99	<100 – 150	89 750	0.01
TOTAL				811

 Table 13. 3: Waste production from PCB production in Turkey

## **BATTERIES AND ACCUMULATORS**

#### 14.1 Objective and Scope

Objective of this chapter is to determine the amount of waste batteries and accumulators generated in Turkey. In EWC and Annex 7 of RCHW of Turkey batteries include lead batteries, Ni-Cd batteries, mercury containing batteries, alkaline batteries, electrolyte from batteries and accumulators [3,19].

## 14.2 Introduction

Waste batteries and accumulators pose a great problem since each year number of batteries and accumulators wasted is very high. But more importantly, recycling and disposal practices for waste batteries and accumulators is nor adequate. Because of the fact that batteries are being collected with municipal solid wastes, estimation of waste batteries is not currently possible. Consequently, only waste accumulators are covered in this section.

14.3 Hazardous Wastes Generated from Batteries and Accumulators

According to EWC and Annex 7 of the RCHW of Turkey waste *lead batteries* (16 06 01), Ni-Cd batteries (16 06 02), mercury containing batteries (16 06 03) and separately collected electrolyte from batteries and accumulators (16 06 06) are classified as absolute entries [3,19].

- 14.4 Information Required for Determining Hazardous Waste Generation from Batteries and Accumulators
  - 1 **Number of each type of accumulator wasted each year**: It was not possible to determine the amounts of each type of accumulators wasted in Turkey.
  - 2 Number of vehicles in Turkey: Since information could not be obtained for different types of batteries and accumulators wasted, another approach is used for waste vehicle accumulators. In this approach, number of vehicles is multiplied with a waste generation factor. The number of vehicles in turkey is given in Table 14. 1 [89].
  - 3 **Total amount of accumulators present in each type of vehicle:** Average accumulator mass present in vehicles is given in Table 14. 1.

Vehicle	Number of vehicles [83]	Average accumulator mass (kg) [89]	Total mass (kg)
Motorcycle	1,046,499	3	3,139,497
Automobile	5,624,046	15	84,360,690
Minibus	330,064	15	4,950,960
Bus	158,331	58	9,183,198
Pickup truck	1,380,925	15	20,713,875
Truck	663,112	42	27,850,740
Tractor	1,231,356	28	34,477,968
TOTAL	10,434,333		184,136,928

Table 14. 1: Total amount of accumulators present in vehicles

- 4 **Contents of accumulators**: Approximately vehicle accumulators contain 65% of lead and lead compounds, 30% sulfuric acid and 5% plastic by weight [89]. It is estimated that 1/3of the vehicles have their accumulator changed in a year [89].
- 5 Hazardous waste generation factor for waste accumulators: It is assumed that 1/3 of vehicles have their accumulators changed each year [89].

14.5 Hazardous Waste Generation from Waste Batteries and Accumulators

According to Section 14.4 there exist nearly 10.5 million accumulators and based on percent of materials found in accumulators 120,250 tons of lead, 55,500 tons of sulfuric acid and 9,250 tons of plastic material in the accumulators in the year 2005 [89].

Based on the assumption that 1/3 vehicles have their accumulator changed in a year, 3.5 million accumulators are wastes in 2005 which leads to disposal of 40,000 tons of lead, 18,500 tons of sulfuric acid and 3,000 tons of plastic material.

Results obtained for 2-digit entry of 16 is given in Table 14. 2.

Name of the entry		Amo	unt generate	ed (t/yr)	
2-digit	4-digit	6-digit	6-digit	4 digit	2 digit
		End-of-life vehicles (16 01 04)			
		<i>Oil filters (16 01 07)</i>			
	End-of-life vehicles from	<i>Components containing mercury (16 01 08)</i>			
	<i>different means of transport</i> (including off-road	Components containing PCBs (16 01 09)			
	(including off-road machinery)	Explosive components (16 01 10)			
	and wastes from	Brake pads containing asbestos (16 01 11)			63,800 – 64,920
	dismantling of end-of-life	Brake fluids (16 01 13)			
W	vehicles and vehicleWastes notmaintenance (16 01)otherwisespecified in the	Antifreeze fluids containing dangerous substances (16 01 04)			
otherwise specified in the		Hazardous components other than those mentioned in 16 01 07 to 16 01 11 and 16 01 13 and 16 01 14 (16 01 21)			
list (16) Wastes from electrical a electronic equipment (16 02)		<i>Transformers and capacitors containing</i> <i>PCBs</i> (16 02 09)			
	Wastes from electrical and	Discarded equipment containing or contaminated by PCBs other than those mentioned in 16 02 09 (16 02 10)		011	
		Discarded equipment containing chlorofluorocarbons, HCFC, HFC (16 02 11)		811	
		Discarded equipment containing free asbestos (16 02 12)			

## Table 14. 2: Results obtained for wastes not otherwise specified in the list (16)

Name of the entry				unt generat	ed (t/yr)
2-digit	4-digit	6-digit	6-digit	4 digit	2 digit
	Wastes from electrical and electronic equipment (16	Discarded equipment containing hazardous components other than those mentioned in 16 02 09 to 16 02 12 (16 02 13)		811	- 63,800 - 64,920
	02)	Hazardous components removed from discarded equipment (16 02 15)			
	Off-specification batches	Inorganic wastes containing dangerous substances (16 03 03)			
	and unused products (16 03)	Organic wastes containing dangerous substances (16 03 05)			
	Waste explosives (16 04) Gases in pressure containers and discarded chemicals (16 05)	Waste ammunition (16 04 01)			
Wastes not		Fireworks wastes (16 04 02)			
otherwise		Other waste explosives (16 04 03)			
specified in the ist (16)		Gases in pressure containers (including halons) containing dangerous substances (16 05 04)			
		Laboratory chemicals, consisting of or containing dangerous substances, including mixtures of laboratory chemicals (16 05 06)			
		Discarded inorganic chemicals consisting of or containing dangerous substances (16 05 07)			
		Lead batteries (16 06 01)			
	Batteries and accumulators	Ni-Cd batteries (16 06 02)			
		Mercury-containing batteries (16 06 03)		61,500	
	(16 06)	Separately collected electrolyte from batteries and accumulators (16 06 06)			

## Table 14. 2 continued

	Name of the entry				ed (t/yr)
2-digit	4-digit	6-digit	6-digit	4 digit	2 digit
s c (	Wastes from transport tank,	Wastes containing oil (16 07 08)			
	storage tank and barrel cleaning (except 05 and 13) (16 07)	Wastes containing other dangerous substances (16 07 09)		]	
		Spent catalysts containing dangerous transition metals or dangerous transition metal compounds (16 08 02)			63,800 – 64,920
	Spent catalysts (16 08)	Spent catalysts containing phosphoric acid (16 08 05)		240 – 734	
otherwise		Spent liquids used as catalysts (16 08 06)	10		
specified in the list (16)		Spent catalysts contaminated with dangerous substances (16 08 07)	230 - 724		
	Oxidizing substances (16 09)	Permanganates, for example potassium permanganate (16 09 01)			
		Chromates, for example potassium chromate, potassium or sodium dichromate (16 09 02)			
		<i>Peroxides, for example hydrogen peroxide (16 09 03)</i>		]	
		Oxidizing substances, not otherwise specified (16 09 04)			

Table 14. 2 continued

	Name of the entry				ed (t/yr)
2-digit	4-digit	6-digit	6-digit	4 digit	2 digit
Aqueous liquid wastes destined for off-site treatment (16 10)Wastes not otherwise specified in the list (16)Waste linings and refractories (16 11)		Aqueous liquid wastes containing dangerous substances (16 10 01)			
	Aqueous concentrates containing dangerous substances (16 10 03)				
	Waste linings and refractories (16 11) metal substa Lining metal	Carbon-based linings and refractories from metallurgical processes containing dangerous substances (16 11 01)	 1260 - 1870 1260 - 1870		
		Other linings and refractories from metallurgical processes containing dangerous substances (16 11 03)			
		Linings and refractories from non- metallurgical processes containing dangerous substances (16 11 05)		1870	
		Spent catalysts contaminated with dangerous substances (16 08 07)			

## Table 14. 2 continued

# WASTES FROM HUMAN OR ANIMAL HEALTH CARE AND/OR RELATED RESEARCH

#### 15.1 Objective and Scope

Objective of this chapter is to determine the amount of hazardous wastes generated from hospitals.

15.2 Hazardous Wastes Generated from Human or Animal Health Care and/or Related Research

Wastes from human or animal heath care and/or related research (18) has two 4-digit entries that are wastes from natal care, diagnosis, treatment or prevention of disease in humans (18 01) and wastes from research, diagnosis, treatment or prevention of disease involving humans (18 02) [3,19].

Wastes from natal care, diagnosis, treatment or prevention of disease in humans (18 01) which is the only 4-digit entry covered in this thesis contain four 6-digit entries that are wastes whose collection and disposal is subject to special requirements in order to prevent infection (18 01 03), cytotoxic and cytostatic medicines (18 01 08), amalgam waste from dental care (18 01 10) and chemicals consisting of or containing dangerous substances (18 01 06). The first three are classified as absolute entries while the last one is a minor entry [3,19].

Wastes from research, diagnosis, treatment or prevention of disease involving humans (18 02) contain wastes whose collection and disposal is subject to special requirements in order to prevent infection (18 02 02), cytotoxic and cytostatic medicines (18 02 07) as absolute entries and chemicals consisting of or containing dangerous substances (18 02 05) as a minor entry.

- 15.3 Information Required for Determining Hazardous Wastes Generated from Human or Animal Health Care and/or Related Research
  - Capacities of hospitals in terms bed numbers: There exits 683 hospitals under Ministry of Health, 146 are SSK hospitals, 52 are university hospitals, 278 are private hospitals and 58 are other public hospitals [90] which leads to a total number of 1,217. The number of beds in the hospitals are given in Table 15. 3.

According to data given in Table 15. 3, Table 15. 1 is prepared.

	Number of beds
Hospitals under Ministry of Health	96,466
SSK hospitals	20,621
University hospitals	7,345
Other public hospitals	8,192
Private hospitals	39,264
TOTAL	171,888

Table 15. 1: Number of beds in terms of hospitals

- 2 Waste generation factors related to hazardous wastes generated from hospitals: Waste generation factors given in literature related to hospital wastes are given in Section 15.4.
- 15.4 Hazardous Waste Generation Factors for Wastes Generated from Human or Animal Health Care and/or Related Research

According to a study conducted by Demir et al. waste generation factors for hospital wastes are specified as given in Table 15.2[91].

	Waste generation factors (kg/day/bed)
Hospitals under Ministry of Health	0.51
SSK hospitals	0.62
University hospitals	1.24
Other public hospitals	0.2
Private Hospitals	0.8

 Table 15. 2: Waste generation factors for wastes originating from hospitals [91]

Province	Number of beds <sup>*</sup>	Province	Number of beds <sup>*</sup>	Province	Number of beds <sup>*</sup>	Province	Number of beds <sup>*</sup>
Adana	4,910	Edirne	1,262	Kütahya	1,282	Uşak	794
Adıyaman	806	Elazığ	2,367	Malatya	1,581	Van	1,413
Afyonkarahisar	2,147	Erzincan	652	Manisa	3,038	Yozgat	978
Ağrı	293	Erzurum	3,103	Kahramanmaraş	1,419	Zonguldak	2,304
Amasya	810	Eskişehir	3,032	Mardin	587	Aksaray	800
Ankara	16,116	Gaziantep	2,372	Muğla	1,632	Bayburt	100
Antalya	3,021	Giresun	1,268	Muş	612	Karaman	515
Artvin	581	Gümüşhane	356	Nevşehir	515	Kırıkkale	1,023
Aydın	1,813	Hakkari	170	Niğde	735	Batman	294
Balıkesir	2,630	Hatay	1,636	Ordu	183	Şırnak	235
Bilecik	278	Isparta	2,713	Rize	820	Bartın	413
Bingöl	531	Mersin	3,178	Sakarya	1,372	Ardahan	155
Bitlis	524	İstanbul	35,120	Samsun	3,697	Iğdır	180
Bolu	1,280	İzmir	11,030	Siirt	370	Yalova	364
Burdur	671	Kars	363	Sinop	560	Karabük	763
Bursa	5,263	Kastamonu	1,476	Sivas	2,615	Kilis	190
Çanakkale	1,048	Kayseri	2,669	Tekirdağ	1,296	Osmaniye	578
Çankırı	600	Kırklareli	726	Tokat	1,582	Düzce	922
Çorum	1,632	Kırşehir	551	Trabzon	2,828		
Denizli	1,420	Kocaeli	2,419	Tunceli	140	TOTAL	171 888
Diyarbakır	2,784	Konya	3,547	Şanlıurfa	1,760		

Table 15. 3: Bed numbers in provinces of Turkey [90]

\* based on 2004 population

According to Demir et al. 45% of these wastes generated in hospitals can be classified as hazardous [91].

15.5 Hazardous Waste Generation Human or Animal Health Care and/or Related Research Wastes

According to data given Table 15. 1 and waste generation factors tabulated in Table 15.2, results given in Table 15. 4 are obtained.

	Waste generation (t/yr)	Hazardous waste generation (t/yr)
Hospitals under Ministry of Health	18,000	8,080
SSK hospitals	4,650	2,100
University hospitals	3,320	1,500
Other public hospitals	600	270
Private Hospitals	11,465	5,160
TOTAL	38,035	17,100

Table 15. 4: Hazardous waste generation from hospitals in Turkey

	Name of the entry			nt generated	l (t/yr)	
2-digit	4-digit	6-digit	6-digit 4 digit		2 digit	
Wastes from Human and Animal Health Care and/or Related Research (18)	Wastes from natal care,	Wastes whose collection and disposal is subject to special requirements in order to prevent infection (18 01 03)			17,100	
	diagnosis, treatment or prevention of disease in	Chemicals consisting of or containing dangerous substances (18 01 06)		17,100		
	Wastes from research, diagnosis, treatment or prevention of disease involving animals (18 02)	<i>Cytotoxic and cytostatic medicines</i> (18 01 08)				
		Amalgam waste from dental care (18 01 10)				
		Wastes whose collection and disposal is subject to special requirements in order to prevent infection (18 02 02)				
		Chemicals consisting of or containing dangerous substances (18 02 05)				
	involving animals (1802)	<i>Cytotoxic and cytostatic medicines</i> (18 02 07)				

Table 15. 5: Results obtained wastes from human and animal health care and/or related research (18)

## WASTES FROM INCINERATION OR PYROLYSIS OF WASTE

#### 16.1 Objective and Scope

Objective of this chapter is to determine the amount of hazardous wastes generated from waste management facilities, off-site wastewater treatment plants, and the preparation of water intended for human consumption and water for industrial use. Attention was given to incineration of wastes due to lack of information on other treatment facilities in Turkey.

### 16.2 Introduction

According to EWC and Annex 7 of RCHW of Turkey, this heading covers incineration and pyrolysis of waste, physico/chemical treatment of wastes, stabilization/solidification of wastes, vitrification, aerobic and anaerobic treatment, water treatment plants, preparation of water intended for human consumption, shredding of wastes, oil regeneration, mechanical treatment of wastes and finally, soil and groundwater remediation.

16.3 Hazardous Wastes Generated from Incineration of Wastes

Wastes from incineration or pyrolysis of waste (19 01) is a 4-digit entry which is under wastes from waste management facilities, off-site water treatment plants and the preparation of water intended for human consumption and water for industrial use(19). This 4-digit entry includes four 6-digit absolute entries; filter cake from gas treatment (19 01 05), aqueous liquid waste from gas treatment and other aqueous liquid wastes (19 01 96), solid wastes from gas treatment (19 01 07) and spent activated carbon from flue-gas treatment (19 01 10). Besides these, minor entries include bottom ash and slag (19 01 11), fly ash (19 01 13), boiler dust (19 01 15) and pyrolysis wastes (19 01 17) that contains dangerous substances [3,19].

16.4 Information Required for Determining Hazardous Wastes Generated from Incineration of Wastes

Information required for determination of hazardous waste generation from organic chemical processes can be listed as follows:

 Capacity information related to incineration facilities: Currently there are two hazardous waste incinerators in Turkey; namely İZAYDAŞ located in İzmit and Petkim Hazardous Waste Incinerator located in Aliağa, İzmir. Approximately 3,900 tons/year of solid waste is incinerated in PETKİM in the year 2004. Amounts of hazardous wastes incinerated in İZAYDAŞ are given in Table 16.
 In İZAYDAŞ lime scrubber is being used for flue gas cleaning.

 Table 16. 1: Hazardous waste amounts incinerated in İZAYDAŞ [92]

Year	1997	1998	1999	2000	2001	2002	2003	2004
Amount (ton)	1,505	8,018	4,785	13,903	14,002	10,024	19,450	10,775*

<sup>\*</sup> Data is upto 31.10.2004

2 Hazardous waste generation factors for waste incinerators: Waste generation factors for incinerators are given in Section 16.5.

16.5 Hazardous Waste Generation Factors for Waste Incinerators

In Table 16. 2 quantities of main waste streams are given. Besides these wastes, waste generation factors for aqueous wastes from scrubber should be known. Typical quantities of scrubbing water arising from the flue-gas cleaning of waste incineration plants are tabulated in Table 16. 3.

	Residue production (kg/t of waste input)				
	Minimum	Maximum	Average		
Bottom ash	83	246	140		
Boiler ash + fly ash + solid flue gas cleaning residue	32	177	74		
Filter cake from Effluent Treatment Plant (ETP)	9	83	30		
Dust			0.0098		

 Table 16. 2: Quantities of main waste streams from hazardous waste incineration [93]

Table 16. 3: Typical values of the amount of scrubbing water arising from flue gas treatment at
waste incineration plants [93]

Plant type and waste throughput	Type of flue gas cleaning	Approx. quantity of wastewater (m <sup>3</sup> /t waste)
Municipal waste incineration plant with a throughput of 250,000 t/yr	2 stages, with milk of lime	0.15 (design value)
Municipal waste incineration plant with a throughput of 250,000 t/yr	2 stages, with sodium hydroxide (before condensation facility)	0.3 (operating value)
Hazardous waste incineration plant with a throughput of 60,000 t/yr	2 stages, with milk of lime	0.15 (annual average)
Hazardous waste incineration plant with a throughput of 30,000 t/yr	2 stages, with sodium hydroxide	0.2 (annual average)

## 16.6 Hazardous Waste Generation from Waste Incineration

According to information obtained from PETKİM the total amount of ash is 212 tons/year and the amount of slag is 454 tons/year .Moreover, according to waste generation factors obtained from Draft Reference Document on Best Available Techniques for Waste Incineration 38.22 kg of dust and 780 m<sup>3</sup> of wastewater are generated from this incinerator. Therefore, a total of approximately 780 tons of hazardous wastes are generated from the incinerator in PETKİM with 666 tons of

possible hazardous wastes (assuming the density of generated scrubbing water as  $1 t/m^3$ ).

The average amount of hazardous wastes originating from İZAYDAŞ is given in Table 16. 4.

	Amount (Tons/day)	Amount (Tons/year)
Filter cake	8.3	3,030
Fly ash	1.1	400
Bottom ash	14.4	5,260
Dust		0.12
Wastewater		1,940
TOTAL		10,630

 Table 16. 4: Hazardous wastes originating from İZAYDAŞ [92]

It can be concluded that from İZAYDAŞ 5616.7 tons of absolute entries and 5657.5 tons of minor entries are produced. Finding regarding the 2-digit entry of *19* is given in Table 16. 5.

## 16.7 Comments

Although waste incineration is not the only waste treatment from which hazardous wastes are generated no adequate information could be obtained especially for capacities of other waste treatment facilities.

Name of the entry	Amount generated (t/yr)		
2-digit 4-digit 6-digit	6-digit	4 digit	2 digit
2-digit4-digit6-digitWastesFilter cake from gas treatment (19 01 05)WastesManagement Facilities, Off-site Waste Water Treatment Plants and the Preparation of Waster Intended for Human Consumption and Water for Industrial Use (19)Wastes from incineration or pyrolysis of waste (19 01)Wastes fromWastes from incineration or pyrolysis of waste (19 01)Solid wastes from gas treatment (19 01 07)Bottom ash and slag containing dangerous substances (19 01 10)Bottom ash and slag containing dangerous substances (19 01 13)Boiler dust containing dangerous substances (19 01 15)Boiler dust containing dangerous substances (19 01 15)Pyrolysis wastes containing	3,030       2720       5930       400	11,600	112,380 – 316,400 t/yr

# Table 16. 5: Results obtained for wastes from incineration or pyrolysis of waste

# MUNICIPAL WASTES INCLUDING SEPARATELY COLLECTED FRACTIONS

#### 17.1 Objective and Scope

Objective of this chapter is to determine the amount of hazardous wastes generated from municipal sources.

#### 17.2 Introduction

Many of the products used around the home everyday such as household cleaners, personal products, automotive products, print products, and garden products are toxic and can be hazardous to health and the environment [1]. Typical hazardous household products can be household cleaners (chlorine bleach, shoe polish toilet bowl cleaner etc.), personal care products (nail polish remover, medicated shampoos etc.), automotive products (antifreeze, car batteries waste oil etc.), paint products, miscellaneous products such as batteries, photographic chemicals and pesticides, herbicides and fertilizers used in everyday life [1].

The hazardous wastes produced by commercial establishments are related primarily to the service provided [1]. Typical examples include wastes from print shops, solvents from dry cleaning which are listed under different entries in EWC and Annex 7 of the RCHW of Turkey.

17.3 Hazardous Wastes Generated from Municipal Sources

Under *Municipal Wastes (20)* given in Appendix B, there is only one 4-digit entry that contains absolute and minor entries, *separately collected fractions (2001)*. 20

01 includes solvents (20 01 13), acids (20 01 14), alkalines (20 01 15), photochemicals (20 01 17), pesticides (20 01 19), fluorescent tubes and other mercury containing waste (20 10 21) and cytotoxic and cytostatic medicines (20 01 31) [3,19].

Although in European Waste Catalogue and Annex 7 of the Regulation on Control of Hazardous Wastes of Turkey, municipal hazardous wastes are classified under different entries, waste generation factors could not be found for each. However, it is possible to estimate the total municipal hazardous waste generation (20 01).

- 17.4 Information Required for Determining Hazardous Waste Generation from Municipal Sources
  - 1 Population information: Turkey's population should be known in order to estimate hazardous waste generation from municipal sources. According to State Statistics Institute's demographic statistics dating 2000, population of Turkey is 67 844 903.
  - 2 Waste generation factor for municipal hazardous waste generation: In Management of Hazardous Wastes Project Final Report domestic solid waste generation rate is assumed as 0.65 kg/capita/day which will be adopted in calculations for municipal hazardous waste generation [12]. Moreover, according to Management of Hazardous Wastes Project Final Report hazardous fraction in domestic solid waste is estimated to be 0.3% [12]. Approximately 75 85% of the hazardous wastes found in municipal solid waste are from residential sources [12].

#### 17.5 Hazardous Waste Generation from Municipal Sources

According to State Statistics Institute's demographic statistics dating 2000, population of Turkey is 67 844 903. Therefore, yearly solid waste generation across Turkey is approximately 161 million tons. Since 0.3% of this waste is assumed to be hazardous, total hazardous waste generation from domestic source turns out to be 48,300 tons/yr. It is estimated that 75 – 85% of municipal hazardous wastes are originating from domestic source which leads to 64,400– 57,600 tons of municipal hazardous wastes.

## SUMMARY OF RESULTS AND DISCUSSION

Results obtained from calculations done for covered entries are summarized in Table 18. 1. In this table data is arranged in terms of main industrial activities or major sources of generation. Total hazardous waste generation calculated in previous chapters is presented in this table along with their entry numbers and type of that entry. It can be seen from the table that total hazardous waste generation for covered entries in Turkey is in the range of 4,940,000 - 5,110,000 t/yr.

In Table 18. 2, distribution of total hazardous waste generation in terms of absolute and minor entries is given for each 2-digit entry given in EWC and Annex 7 of RCHW of Turkey. It can be seen from Table 18. 2 that, two major waste sources of minor wastes are tailings and FGD wastes. Throughout the thesis, it is discussed that wastes generated as minor entries need to be analyzed for the potential of being hazardous. Given that the total amount of tailings and FGD wastes have a high percentage in total amount of hazardous wastes generated in Turkey, in the rest of the discussion two cases will be considered. First one is the case in which all of the tailings and FGD wastes are assumed to be hazardous. This case presents the highest amount of hazardous wastes are excluded from the calculations. Given that all of these wastes may not be hazardous, this case presents the minimum hazardous waste generated in Turkey 2,670,000 – 2,850,000 t/yr are absolute entries and 1,090,000 – 1,150,000 t/yr is minor entries.

Entry	Description	Hazardous waste generated	Type of entry
Mining activ	vities	·	
01 03 04 or	Potential of tailings to be hazardous should be analyzed	2,118,000 t/yr	Absolute
01 03 05			Minor
Wood prese	rvation		
03 02 01			Absolute
03 02 02	Average waste generation for three types of wood preservatives	680,000 t/yr	Absolute
03 02 03			Absolute
Petroleum r	efining		
05 01 02	Desalter sludge	240 – 6,000 t/yr	Absolute
05 01 03	Tank bottom sludges (from distillation and storage)	200,000 – 219,000 t/yr	Absolute
05 01 09	Sludge from wastewater treatment plant	12,500 t/yr	Minor
16 08 07	Spent catalysts	131.2 – 164 t/yr	Minor
TOTAL 213		213,500 – 237,800 t/yr	
Mfsu of acid	ls		
06 01 01 or	Sulfuric or nitric acid containing wastewaters	70,000 t/sm	Abaaluta
06 01 05	from DNT and TNT production	70,000 t/yr	Absolute
06 01 01	Sulfuric acid containing from nitrocellulose production	1,500 t/yr	Absolute
06 01 01 or	Sulfuric or nitric acid containing from nitroglycerine production	55,300 – 235,000 t/yr	Absolute
06 01 05			
06 01 01	Sulfuric acid from halogen production	6000 – 8575 t/yr	Absolute
16 08 06	Spent catalyst from sulfuric acid production	10 t/yr	Absolute
TOTAL	·	131,000 – 315,000 t/yr	

 Table 18. 1: Summary of calculations (for entries covered)

Entry	Description	Hazardous waste generated	Type of entry
Petrocher	nicals industry	·	
07 02 01	Aqueous washing liquid and mother liquids (from ACN production)	31,000– 80,000 t/yr	Absolute
07 02 07	Halogenated still bottoms an reaction residues (from VCM and PVC production)	380 t/yr	Absolute
07 02 08	Other still bottoms and reaction residues (from ethylene, ACN, VCM, PP, styrene butadiene rubber, polystyrene production)	48,300 – 184,400 t/yr	Absolute
06 01 06	HCN (from ACN production)	8,000 – 10,500 t/yr	Absolute
16 08 07	Spent catalysts (from ethylene, EG/EO, ACN, VCM production)	100 – 560 t/yr	Minor
TOTAL		87,800 – 275,900 t/yr	
Thermal	processes		
10 01 18	Gypsum from power plants	999,200 t/yr	Minor
10 03 15	Al skimmings from aluminum thermal metallurgy	1,300 – 1,900 t/yr	Minor
16 11 03	SPL from aluminum thermal metallurgy	1,230 – 1,840 t/yr	Minor
	Other hazardous wastes	430 – 920 t/yr	
10 03 08	Salt slag from secondary aluminum production	7,425 t/yr	Absolute
10 03 21	Filter dust from pyrometallurgical aluminum production	520 t/yr	Minor
16 11 03	Furnace lining from secondary aluminum production	30 t/yr	Minor
10 13 19	Dust from pyrometallurgical aluminum production	4,455 – 10,400 t/yr	Minor
10 04 01	Slags from pyrometallurgical lead production	4,100 – 4,200 t/yr	Absolute
10 04 04	Flue dust from pyrometallurgical lead production	55 – 640 t/yr	Absolute
10 04 02	Dross from pyrometallurgical lead production	620 – 750 t/yr	Absolute
10 06 03	Dust from pyrometallurgical copper production	15,250 t/yr	Absolute
TOTAL		1,034,600 – 1,043,000 t/yr	

Table 18. 1 Continued

Entry	Description	Hazardous waste generated	Type of entry		
Metal coating industry					
11 01 05	Pickling acids	1,210 – 61,200 t/yr	Absolute		
11 01 13	Degreasing wastes (cleaning agents)	120 – 5,450 t/yr	Minor		
TOTAL		1,330 – 66,650 t/yr			
Waste oils					
13 02	Waste engine oils	290,000 t/yr	Absolute		
13 03	Transformer oils	1,000 t/yr	Absolute		
13 01 01	PCB containing transformer oils	25 000 liters *	Minor		
TOTAL		291,000 t/yr			
Waste sol	vents				
14 06 03	Wastes from printing industry	212,530 t/yr	Absolute		
14 00 05		41,000,000 items/yr			
14 06 05	Wastes from dry cleaning industry	14,240 – 28,470 t/yr	Absolute		
06 13 02	Activated carbon from printing processes	2,900 t/yr	Minor		
TOTAL		229,670 – 243,900 t/yr			
Wastes fr	om PCB manufacture				
11 01 05	Acidic pickling agents from PCB manufacture	270 t/yr	Absolute		
11 01 07	Alkaline pickling agents from PCB manufacture	225 t/yr	Absolute		
11 01 09	Sludges from PCB manufacture	315 t/yr	Minor		
11 01 99	Precious metals/metals	0.01 t/yr	Minor		
TOTAL		810 t/yr			

Table 18. 1 Continued

Amount collected up to the year 2002

Entry	Description	Hazardous waste generated	Type of entry
Waste acc	umulators		
16 06 01	Waste accumulators	3.5 million accumulators containing 40,000 t/yr of lead 18,500 t/yr of sulfuric acid 3,000 t/yr of plastic material	Absolute
Wastes fr	om hospitals		
18 01 03		17,100 t/yr	Absolute
Wastes fr	om hazardous waste incineration		•
19 01 06	Aqueous liquid wastes from incineration	2850 t/yr	Absolute
19 01 05	Filter cake	3,030 t/yr	Absolute
19 01 11	Slag and bottom ash	5,260 t/yr	Minor
19 01 13	Fly ash	615 t/yr	Minor
TOTAL		11,625 t/yr	
Municipa	hazardous wastes		
20 01		64,400– 57,600 t/yr	Absolute
TOTAL (including tailings)		10,523,000 – 10,764,000 <sup>*</sup> t/yr	
TOTAL (excluding tailings)		3,205,000 – 3,445,000 t/yr	

Table 18. 1 Continued

\* Average density of wood preservatives is assumed to be 2,5 kg/L

Average density of waste engine oils is assumed to be 0.890 kg/L Average density of waste solvents, aqueous liquid wastes from incinerators and acidic liquid wastes from explosives manufacture is assumed to be 1,05 kg/L
	RCHW of Turkey		
2-digit entry code	Absolute entries	Minor entries	
	(t/yr)	(t/yr)	
01		2,118,000	
03	680,000		
05	200,240 - 225,000	12,630 - 12,670	
06	132,810 - 315,000		
07	87,700 - 275,300	100 - 550	
10	31,900 - 38,300	1,607,000 - 1,013,900	
12	1,210 - 61,200	120 - 5,450	
13	291,000		
14	226,800	2,900	
16	62,000	315	
18	17,100		
19	5,900	5,260	
20	57,600 - 64,400		
TOTAL		4,940,000 - 5,410,000	
TOTAL (excluding tailings		1 920 000 2 205 000	
and FGD wastes)		1,820,000 - 2,295,000	
TOTAL	1,790,000 - 2,252,000	3,146,000 - 3,160,000	
TOTAL (excluding tailings and FGD wastes)	1,790,000 - 2,252,000	1,028,000 - 1,041,000	

Table 18. 2: Absolute and minor entries generated from 2-digit entries of EWC and Annex 7 of RCHW of Turkey

In terms of contribution of 2-digit entries to total hazardous waste generation; when both tailings and FGD wastes are included in estimations, highest generation seems to occur from the 02 Category that is *wastes resulting from exploration, mining, quarrying, and physical and chemical treatment of minerals* with a percentage of 40.7 %. When tailings are excluded considering that they are minor entries, highest generation turns out to be from the Category 10 - *wastes from thermal processes* producing 33.7% of total hazardous wastes. When both tailings and FGD wastes are excluded from the calculations, highest generation source proves to be wood preservation (03) with a percentage of 32.6%. However, given that some portion of tailings and FGD wastes may be hazardous, wood preservation may not be the source of highest generation. Again this proves the fact that tailings and FGD wastes should be analyzed for the potential of being hazardous to have a complete understanding of distribution hazardous wastes in terms of 2-digit entries.

Besides the total generation amount, another important point to be considered in relation to the management is the geographical distribution of hazardous wastes in Turkey. To be able to assess this issue, generation point of all the hazardous waste should be known. For point sources such as petroleum refining or petrochemical complexes, the amount of hazardous wastes generated could be easily assigned to the province in which these facilities are located. For some other wastes such as wood preservation or printing industry, the distribution of industry throughout Turkey is identified. The most helpful tool for this identification was the industrial database of TOBB [34]. By referring this database distribution of the industry in terms of province is obtained and hazardous wastes generated from those industries are assigned to provinces based on the extent of industry in that province.

Last group of hazardous wastes are the ones generated throughout the country. Examples of these groups are dry cleaning industry, waste accumulators, municipal hazardous wastes and wastes from hospital. For dry cleaning industry, secondary aluminum and lead production and finally municipal hazardous waste generation, factors for each province were calculated based on their shares in total population. For waste oils and waste accumulators, factors are calculated in terms of vehicle numbers. The number of each type of vehicle in each province is determined and waste oils are assigned to provinces depending on the number of each vehicle in a given province.

After hazardous waste generation from each province is determined regional hazardous waste generation is calculated. Figure 18. 1 and Table 18. 3 presents the regional distribution of hazardous wastes produced in Turkey.



**(a)** 



**(b)** 

Figure 18. 1 (a) Regional distribution of hazardous wastes (including tailings and FGD wastes) (b) Regional distribution of hazardous wastes (excluding tailings and FGD wastes)

Region	Hazardous waste generation	Hazardous waste generation (excluding tailings and FGD wastes)	% share	% share (excluding tailings and FGD wastes)
Aegean	941,950	524,580	18.1	24.8
Mediterranean	885,200	211,580	17.0	10.0
Central Anatolia	1,026,370	481,820	19.7	22.7
Marmara	1,012,060	527,730	19.5	24.9
Black Sea	730,810	277,850	14.1	13.1
Eastern Anatolia	382,220	36,520	7.3	1.7
Southeast Anatolia	222,330	58,290	4.3	2.8
TOTAL	5,200,000	2,118,300	100.0	100.0

Table 18. 3: Regional hazardous waste generation and distribution

Figure 18.1 shows variation in order of regional distribution of hazardous wastes. When tailings and FGD wastes are considered along with other hazardous wastes, Central Anatolia Region seems to be the highest generator with a percentage of 19.7%, followed by Marmara Region (19.5%) and Aegean Region (18.1%). Lowest amount of hazardous wastes are generated from Eastern Anatolia (7.3%) and Southeast Anatolia (4.3%) when tailings and FGD wastes are included in calculations. When these two groups of wastes are omitted from the estimations the order differs. In the case of excluding tailings and FGD wastes highest generator proves to be Marmara Region (24.9%) followed closely by Aegean Region (24.8%). In this situation, Central Anatolia is the third highest generator with a share of 22.7%. There is a sharp decrease in shares of Mediterranean and Eastern Anatolia. This is due to the fact that in Mediterranean Region highest generation occurs from thermal processes and in Eastern Anatolia highest generation occurs from mining activities.

Following figures aims to present the distribution of hazardous wastes in each region with and without tailings and FGD wastes. In these figures, hazardous waste generation is plotted versus 2-digit entries of EWC and Annex 7 of RCHW of Turkey.







**(b)** 

Figure 18. 2: (a) Distribution of hazardous wastes in Aegean region (including tailings and FGD wastes)
(b) Distribution of hazardous wastes in Aegean region (excluding tailings and

FGD wastes)







**(b)** 

Figure 18. 3: (a) Distribution of hazardous wastes in Mediterranean region (including tailings and FGD wastes) (b) Distribution of hazardous wastes in Mediterranean region (avaluding tailings

(b) Distribution of hazardous wastes in Mediterranean region (excluding tailings and FGD wastes)



(a)



**(b)** 

Figure 18. 4:(a) Distribution of hazardous wastes in Central Anatolia region (including tailings and FGD wastes)

(b) Distribution of hazardous wastes in Central Anatolia region (excluding tailings and FGD wastes)







**(b)** 

Figure 18. 5:(a) Distribution of hazardous wastes in Marmara region (including tailings and FGD wastes)
 (b) Distribution of hazardous wastes in Marmara region (excluding tailings and FGD wastes)







**(b)** 

Figure 18. 6:(a) Distribution of hazardous wastes in Black Sea region (including tailings and FGD wastes) (b) Distribution of hazardous wastes in Black Sea region (excluding tailings and

FGD wastes)



**(a)** 



**(b)** 

Figure 18. 7:(a) Distribution of hazardous wastes in Eastern Anatolia region (including tailings and FGD wastes)
(b) Distribution of hazardous wastes in Eastern Anatolia region (excluding tailings and FGD wastes)







**(b)** 

Figure 18. 8:(a) Distribution of hazardous wastes in Southeast Anatolia region (including tailings and FGD wastes)
 (b) Distribution of hazardous wastes in Southeast Anatolia region (excluding tailings and FGD wastes)

In Figure 18. 2 it can be seen that highest generation occurs from thermal processes (10) and organic chemical processes (07) in Aegean region. When thermal processes and tailings are excluded from the calculation, highest amount of hazardous wastes are produced from organic chemical processes. This high generation figure from organic chemical processes is due to presence of petrochemical industry in İzmir. Other higher generators are wood preservation (03) and petroleum refining (05).

According to Figure 18. 3, highest generation in the Mediterranean Region occurs from thermal processes (10) followed by mining activities (01) and wood preservation (03). When former two are excluded it is seen that wood preservation has the highest contribution to hazardous waste generation in Mediterranean region. The amount of hazardous wastes generated from industrial processes is rather low in this region.

When the Central Anatolia's hazardous waste generation is inspected (Figure 18.4) it is seen that predominant sources of generation are thermal processes (10), mining activities (01) and inorganic chemical processes (06). Share of inorganic chemical processes increases when tailings and FGD wastes are omitted. High generation of hazardous wastes in Central Anatolia region primarily originates from the presence of explosives industry in Ankara and Kırıkkale.

In the region of Marmara, mining activities are the major source of hazardous waste generation as it is given in Figure 18. 5. Hazardous wastes from mining activities are followed by wastes from wood preservation (03), waste oils (13), wastes from petroleum refining (05) and waste solvents (14). Waste oils and waste solvents' share in hazardous waste generation in Marmara Region is as a result of high population in this area. Refinery in İzmit is the main source of hazardous wastes produced as a result of petroleum refining.

Black Sea region is another region in which wastes from industrial sources are low in amounts. It can be seen from Figure 18. 6 that mining activities and wood preservation produce highest amounts of hazardous wastes. When tailings are omitted wood preservation seems to be the leading source of hazardous wastes generation.

When Eastern Anatolia is considered it is seen from Figure 18. 7, except tailings generation there is no significant source of hazardous waste generation.

In Figure 18. 8, it is given that wood preservation and petroleum refining are the major industrial sources of hazardous wastes in Southeast Anatolia region. Moreover,

waste oils generation is higher in this region when compared to the other entries. However, the amounts of hazardous wastes generated are low.

In many references, it is reported that hazardous waste generation in a region or in a country can be related to gross domestic product (GDP) [13]. GDP and GDP originating only from manufacturing industries are compared to the regional distribution of hazardous wastes generation. Table 18. 4 such a comparison which summarizes the shares of regions in hazardous waste generation and GDP is given.

Region	Hazardous waste generation (%)	Hazardous waste generation (%) (excluding tailings and FGD wastes)	GDP (%)	GDP (%) (from manufacturing industry only)
Aegean	18.1	24.8	16	16
Mediterranean	17.0	10.0	12	9
Central Anatolia	19.7	22.7	16	10
Marmara	19.5	24.9	37	53
Black Sea	14.1	13.1	10	7
Eastern Anatolia	7.3	1.7	4	2
Southeast Anatolia	4.3	2.8	5	3
TOTAL	100.0	100.0	100	100

Table 18. 4: Comparison of shares of regions in hazardous waste generation and GDP

In order to show the trends in hazardous waste generation and GDP originating from manufacturing industry, Figure 18.9 is prepared.



(a)



**(b)** 

Figure 18. 9: (a) Comparison of hazardous waste generation and GDP of regions (including tailings and FGD wastes)
(b) Comparison of hazardous waste generation and GDP of regions (excluding tailings and FGD wastes )

It can be seen from Figure 18. 9 that the trends in hazardous waste generation and GDP from manufacturing industry are in accordance. Contributions of regions are in the same order both in hazardous waste generation and GDP. The only difference between hazardous waste generation trend and GDP trend is the predominance of Marmara region in GDP. Although hazardous waste generation in Marmara region seems to be slightly higher than Aegean region, Marmara region's share in GDP is much higher than that of Aegean region's share. Having 53% of GDP, Marmara region is expected to have the highest hazardous waste generation amount followed by Aegean and Central Anatolia regions. However, this difference is not significant in hazardous waste generation.

The contradiction between Marmara region's industrial capacity and hazardous waste generation can be attributed to the entries included in EWC and the RCHW of Turkey for which no calculation could be made due to lack of waste generation factors related to that subject in the literature. According to SIS, İstanbul alone contains 18.8% of all the industrial establishments in Turkey [14]. It is obvious that in terms of industrial capacity, Marmara region's total industrial capacity exceeds the total industrial capacity of all other regions. For instance, for metal shaping and organic chemical processes including cosmetics, soap and detergent, paint, dye and pigment and pharmaceutical industries no waste generation factor could be found therefore, hazardous waste generation could not be determined. Marmara region has the major production in all mentioned sectors when compared to rest of Turkey [34]. According EU figures organic chemical processes has the highest contribution (16%) to hazardous waste generation in EU member states followed by thermal processes (13%). This proves the fact that when organic chemical processes mentioned above are included in calculations it would be seen that Marmara region would produce significantly higher amounts of hazardous wastes compared to other regions.

Another important parameter to be considered is the per capita hazardous waste generation. The results of the estimations indicated that hazardous waste generation in Turkey varies between 30 - 77 kg/capita/yr, where the lower value represents the case in which tailings and FGD wastes are excluded and the higher value represents the case in which these items are included. Per capita generation in EU varies within the range of 23 - 442 kg/capita/yr, the most probable rate being in the range between 40 - 60 kg/capita/yr [13]. When the values of per capita generation in EU and Turkey are compared, it can be seen that they are in accordance. Per capita range of Turkey covers the most probable per capita range of EU. This indicates that the actual per capita generation would fall with in the range of 40 - 60 kg/capita/yr.

In Figure 18.10, per capita hazardous waste generation is shown for each region. Highest per capita hazardous waste generation occurs in Aegean region.

Although, similar amounts of hazardous wastes are calculated to be produced in Aegean and Marmara regions due to high population of Marmara region per capita hazardous waste generation of Marmara region is much lower than Aegean region.



(a)



**(b)** 

Figure 18. 10: (a) per capita hazardous waste generation of regions including tailings and FGD wastes) (b) per capita hazardous waste generation of regions (excluding tailings and FGD

wastes)

At the beginning of the study the aim was to cover both absolute entries and minor entries. However, it became obvious that it is not sufficient to determine the amounts of minor wastes generated. Analysis should be on these wastes to understand whether these wastes are hazardous or not. Since it was not possible to conduct such analysis on samples taken from every source of these wastes mostly absolute entries are covered in this thesis.

Throughout the study some obstacles were encountered. These obstacles are discussed below in an entry-wise manner.

*Wastes from photographic industry (09 01)* is another category for which, adequate information is not present for Turkey. Not only the information about number of facilities, but also the amount of solutions used in photographic industry lacks for Turkey. As a consequence no calculation could be made for photographic waste industry.

Wastes from shaping and physical and mechanical surface treatments of metals and plastics (12 01) include waste entries containing machining oils. Machining oils are used for protection of equipment by minimizing friction throughout shaping of metals and plastics. Like drilling muds they are consumed in a continuous manner therefore, no waste factor could be generated for these materials.

*Waste ammunition, fireworks wastes* and *other waste explosives* are listed in European Waste Catalogue and Annex 7 of the Regulation on Control of Hazardous Wastes of Turkey as absolute entries under entries *16 04 01, 16 04 02* and *16 04 03*. In order to determine the amount of waste explosives generated in Turkey, Turkish General Staff was consulted. However, because of the fact that this information is classified, no data could be obtained.

As in the case of acids and bases, oxidizing substances that are covered under entry *16 09* are used in a variety of chemical processes with varying amounts of usage. No guideline covering all the processes in which oxidizing substances are used, could be found.

In order to estimate the amount of generation rate of tarred products, information was requested from General Directorate of Highways. However, no results could be obtained.

Gathering information about wastewater treatment plants was one of the areas that need to be investigated thoroughly since it is not enough to find the number of wastewater treatment plants. Processes applied in these treatment plants should also be revealed in order to be able to find amount of wastes generated in the scope of *19 02*, *19 03*, *19 04* and *19 08* [19].

Necessity regarding an inventory study is discussed in introduction chapter. However, the results obtained from this study lead to another necessity that is an inventory of industrial facilities and capacities related to these facilities. The most problematic part of this study was to estimate production capacities of small scale industrial facilities. In areas such as metal coating, dry cleaning, wood preservation, organic dyes and pigments formulation, paint and varnish formulation, photographic industry, secondary lead production physical surface treatment of metals, solvent utilizing facilities which largely involves small scale facilities, little or no capacity information could be found. Currently, the only database that gives detailed information enough to conduct a hazardous waste inventory study belongs to TOBB. The only problem associated with TOBB industry database is that, it covers only the facilities that reported their capacities to chambers of their provinces. Moreover, it is not obligatory for facilities to report their capacities to the chambers. Nevertheless, TOBB industry database was one of the most important references used in this thesis. There is a database of industrial facilities at the Ministry of Industry and Trade. However, this database that can be accessed through the website of Ministry, covers only the employee information (i.e. no capacity information is given).

SIS conducted statistical studies on industrial facilities. One of these studies includes percentage rates of capacity utilization in manufacturing industry. In this study, capacity utilization percentages are presented however, total capacities are not given. In another study of SIS goods and services sold by establishments are given along with number of establishments. Unfortunately, capacity information is not given in his study. In addition, information given is based on general industrial groups such as food industry, textile industry etc. However, scope of this thesis in most cases requires a more detailed categorization based on individual production processes. Annual manufacturing industry production and consumption and small scale manufacturing industry statistics of SIS are not available via internet. One last important statistical study of SIS is industrial waste statistics which includes air pollution statistics, municipal wastewater statistics, municipal solid waste statistics, municipal drinking water statistics, mining industry waste statistics, and industrial districts' wastes

statistics [14]. Only the last two items are in the scope of this study however, it was not possible to obtain information detailed enough to assign amount of wastes generated to different entries given in EWC and Annex 7 of the RCHW of Turkey [3,19].

An important outcome of a waste inventory study conducted using theoretical waste generation factors is its potential of being updated. Industry in Turkey is very dynamic meaning that each year industrial capacities are changing. Use of waste generation factors gives opportunity of updating calculations periodically as industrial capacities changes.

In Turkey currently waste declaration forms are being collected by Ministry of Environment and Forestry. Especially hazardous waste generators are unwilling to report the wastes generated to authorities. According to Management of Hazardous Wastes Project Final Report, the number of waste declaration forms collected is far less than the actual number of generators. Another important issue pointed out by Management of Hazardous Wastes Project Final Report is that employees responsible for filling waste declaration reports do not know whether their wastes are hazardous or not. Moreover, many errors are made while filling out the waste declaration forms. It can be concluded that an estimation of hazardous wastes using theoretical factors would give more precise results when compared to an estimation based on reported values.

EWC is recently implemented in RCHW of Turkey. However, it will take time for full implementation of this list. This thesis is an important step for this implementation period since not only hazardous waste generation is studied but also categorization given in EWC and Annex 7 of RCHW of Turkey is used.

# **CHAPTER 19**

# CONCLUSION

In this thesis it is aimed to present hazardous waste inventory of Turkey based on theoretical waste generation factors. Results obtained from the study are summarized as follows:

- Total hazardous waste generation for covered entries in Turkey is 4,940,000 5,110,000 t/yr when tailings and FGD wastes are included. When tailings and FGD wastes are excluded from the calculations it is seen that 1,820,000 2,295,000t/yr of hazardous wastes are being produced in Turkey. Among these wastes 1,790,000 2,252,000 t/yr is absolute entries and 11,028,000 1,041,000 t/yr is minor entries.
- Main difficulty encountered in hazardous waste generation estimation is the lack of industrial capacity information. Databases relate to industrial capacities and production should be constructed.
- When tailings and FGD wastes are considered along with other hazardous wastes, Central Anatolia region seems to be the highest generator with a percentage of 19.7%, followed by Marmara region (19.5%) and Aegean region (18.1%). In the case of excluding tailings and FGD wastes highest generator proves to be Marmara region (24.9%) followed closely by Aegean region (24.8%).Lower generation occurs from Southeast Anatolia and Eastern Anatolia when tailings and FGD wastes are included and excluded respectively.

- Mining activities have the highest contribution to hazardous wastes (40.7%) followed by thermal processes (33.7%) However, when tailings and FGD wastes that comprise high amounts of minor entries are omitted wastes from wood processing generates the highest amount of hazardous wastes.
- It is not possible to estimate the total quantity of minor entries since it is necessary to conduct analysis to understand their potential of being hazardous.
- Hazardous waste generation in Turkey varies between 31.2 76.7 kg/capita/yr, where the lower value represents the case in which tailings and FGD wastes are excluded and the higher value represents the case in which these items are included. Per capita range of Turkey covers the most probable per capita range of EU. Per capita generation is maximum in Aegean Region and minimum in Eastern Anatolia Region.
- Comparison between GDP shares originating from manufacturing industry and hazardous waste generation resulted in similar trends between regions.
- o The only difference between GDP shares and hazardous waste generation is the dominance of Marmara region in GPD followed by Aegean region. However, when hazardous waste generation is considered the amount generated in Marmara region and Aegean region is similar. This difference originates from lack of information on organic chemical processes. Organic chemical processes causes to highest hazardous waste generation in EU member states and organic chemical industry is mainly located in Marmara region.

# **CHAPTER 20**

# **RECOMMENDATIONS FOR FUTURE STUDY**

In this study hazardous waste inventory of Turkey based waste generation factors is presented. Waste generation factors used in this thesis are based on reference documents published by European Union and USEPA. It is no doubt that waste generation factors for Turkey will be different than the factors given in these reference documents due to differences in industrial applications. In further studies, waste generation factors specific to Turkey should be developed for a better estimation of hazardous waste generation. Such studies have to involve either field work or collection of real data from representative industrial facilities. When waste generation factors specific to Turkey is made available, it becomes easier to estimate the hazardous waste generation in the country on a dynamic basis. Of course, a fundamental knowledge required for such a research would be the information on industrial production or industrial capacity as it was fundamental for this thesis.

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# **APPENDIX A**

### Table A. 1: European waste catalogue and hazardous waste list

# EUROPEAN WASTE CATALOGUE AND HAZARDOUS WASTE LIST

Entries with asterisk represent hazardous wastes.

# 01 WASTE RESULTING FROM EXPLORATION, MINING, QUARRYING, AND PHYSICAL AND CHEMICAL TREATMENT OF MINERALS

01	01	, <b>r</b>	• •	
<i>01</i>	01	wastes from	m mineral	excavation
	•			000000000000000000000000000000000000000

01 01 01	wastes from	mineral	metalliferous	excavatio
1 01 01	wastes nom	mmerai	metamicious	CACavallo

01 01 02 wastes from mineral non-metalliferous excavation

01 03	wastes from	physical of	and chemical	processing of	<sup>e</sup> metalliferous	minerals
01 05	musics from	physical	and chemical	processing of	menungerous	minut

- 01 03 04\* acid-generating tailings from processing of sulfide ore
- *01 03 05*\* other tailings containing dangerous substances
- 01 03 06 tailings other than those mentioned in 01 03 04 and 01 03 05
- 01 03 07\* other wastes containing dangerous substances from physical and chemical processing of metalliferous minerals
- 01 03 08 dusty and powdery wastes other than those mentioned in 01 03 07
- 01 03 09 red mud from alumina production other than the wastes mentioned in 01 03 07
- 01 03 99 wastes not otherwise specified

01 04 wastes from physical and chemical processing of non-metalliferous minerals

- 01 04 07\* waste containing dangerous substances from physical and chemical processing of non-metalliferous minerals
- 01 04 08 waste gravel and crushed rocks other than those mentioned in 01 04 07
- 01 04 09 waste sand and clays
- 01 04 10 dusty and powdery wastes other than those mentioned in 01 04 07
- 01 04 11 wastes from potash and rock salt processing other than those mentioned in 01 04 07
- 01 04 12 tailings and other wastes from washing and cleaning of minerals other than those mentioned in 01 04 07 and 01 04 11
- 01 04 13 waste from stone cutting and sawing other than those mentioned in 01 04 07
- 01 04 99 waste not otherwise specified

### 01 05 drilling muds and other drilling wastes

- 01 05 04 freshwater drilling muds and wastes
- 01 05 05\* oil-containing drilling muds and wastes

- 01 05 06\* drilling muds and other drilling wastes containing dangerous substances
- 01 05 07 barite-containing drilling muds and wastes other than those mentioned in 01 05 05 and 01 05 06
- 01 05 08 chloride-containing drilling muds and wastes other than those mentioned in 01 05 05 and 01 05 06
- 01 05 99 wastes not otherwise specified

#### 02 WASTES FROM AGRICULTURE, HORTICULTURE, AQUACULTURE, FORESTRY, HUNTING AND FISHING, FOOD PREPARATION AND PROCESSING

### 02 01 wastes from agriculture, horticulture, aquaculture, forestry, hunting and fishing

- 02 01 01 sludges from washing and cleaning
- 02 01 02 animal-tissue waste
- 02 01 03 plant-tissue waste
- 02 01 04 waste plastics (except packaging)
- animal faeces, urine and manure (including spoiled straw), effluent, 02 01 06 collected separately and treated off-site
- 02 01 07
- waste from forestry
- agrochemical waste containing dangerous substances 02 01 08\*
- agrochemical waste other than those mentioned in 02 01 08 02 01 09
- 02 01 10 waste metal
- 02 01 99 wastes not otherwise specified

## 02 02 wastes from the preparation and processing of meat, fish and other foods of animal origin

- 02 02 01 sludges from washing and cleaning
- 02 02 02 animal-tissue waste
- 02 02 03 materials unsuitable for consumption or processing
- 02 02 04 sludges from on-site effluent treatment
- 02 02 99 waste not otherwise specified

# 02 03 wastes from fruit, vegetables, cereals, edible oils, cocoa, coffee, tea and tobacco preparation and processing; conserve production; yeast and yeast extract production, molasses preparation and fermentation

- 02 03 01 sludges from washing, cleaning, peeling, centrifuging and separation
- 02 03 02 waste from preserving agents
- 02 03 03 wastes from solvent extraction
- 02 03 04 materials unsuitable for consumption or processing
- 02 03 05 sludges from on-site effluent treatment
- 02 03 99 wastes not otherwise specified

### 02 04 wastes from sugar processing

02 04 01 soil from cleaning and washing beet

- 02 04 02 off-specification calcium carbonate
- 02 04 03 sludges from on-site effluent treatment
- 02 04 99 wastes not otherwise specified

# 02 05 wastes from the dairy products industry

- 02 05 01 materials unsuitable for consumption or processing
- 02 05 02 sludges from on-site effluent treatment
- 02 05 99 wastes not otherwise specified

### 02 06 wastes from the baking and confectionery industry

- 02 06 01 materials unsuitable for consumption or processing
- 02 06 02 wastes from preserving agents
- 02 06 03 sludges from on-site effluent treatment
- 02 06 99 waste not otherwise specified

# 02 07 wastes from the production of alcoholic and non-alcoholic beverages (except coffee, tea and cocoa)

- 02 07 01 wastes from washing, cleaning and mechanical reduction of raw materials
- 02 07 02 wastes from spirits distillation
- 02 07 03 wastes from chemical treatment
- 02 07 04 materials unsuitable for consumption or processing
- 02 07 05 sludges from on-site effluent treatment
- 02 07 99 waste not otherwise specified

# 03 WASTES FROM WOOD PROCESSING AND THE PRODUCTION OF PANELS AND FURNITURE, PULP, PAPER AND CARDBOARD

### 03 01 wastes from wood processing and the production of panels and furniture

- 03 01 01 waste bark and cork
- 03 01 04\* sawdust, shavings, cuttings, wood, particle board and veneer containing dangerous substances
- 03 01 05 sawdust, shavings, cuttings, wood, particle board and veneer other than those mentioned in 03 01 04 03 01 99 wastes not otherwise specified

### 03 02 wastes from wood preservation

- 03 02 01\* non-halogenated organic wood preservatives
- 03 02 02\* organochlorinated wood preservatives
- 03 02 03\* organometallic wood preservatives
- 03 02 04\* inorganic wood preservatives
- 03 02 05\* other wood preservatives containing dangerous substances
- 03 02 99 wood preservatives not otherwise specified

# 03 03 wastes from pulp, paper and cardboard production and processing

03 03 01 waste bark and wood

03 03 02 green liquor sludge (from recovery of cooking liquor) 03 03 05 de-inking sludges from paper recycling mechanically separated rejects from pulping of waste paper and 03 03 07 cardboard 03 03 08 wastes from sorting of paper and cardboard destined for recycling 03 03 09 lime mud waste 03 03 10 fibre rejects, fibre-, filler- and coating-sludges from mechanical separation 03 03 11 sludges from on-site effluent treatment other than those mentioned in 0303 10 03 03 99 wastes not otherwise specified

## 04 WASTES FROM THE LEATHER, FUR AND TEXTILE INDUSTRIES

## 04 01 wastes from the leather and fur industry

- 04 01 01 fleshings and lime split wastes
- 04 01 02 liming waste
- 04 01 03\* degreasing wastes containing solvents without a liquid phase
- 04 01 04 tanning liquor containing chromium
- 04 01 05 tanning liquor free of chromium
- 04 01 06 sludges, in particular from on-site effluent treatment containing chromium
- 04 01 07 sludges, in particular from on-site effluent treatment free of chromium
- 04 01 08 waste tanned leather (blue sheetings, shavings, cuttings, buffing dust) containing chromium
- 04 01 09 wastes from dressing and finishing
- 04 01 99 wastes not otherwise specified

### 04 02 wastes from the textile industry

- 04 02 09 wastes from composite materials (impregnated textile, elastomer, plastomer)
- 04 02 10 organic matter from natural products (for example grease, wax)
- 04 02 14\* wastes from finishing containing organic solvents
- 04 02 15 wastes from finishing other than those mentioned in 04 02 14
- 04 02 16\* dyestuffs and pigments containing dangerous substances
- 04 02 17 dyestuffs and pigments other than those mentioned in 04 02 16
- 04 02 19\* sludges from on-site effluent treatment containing dangerous substances
- 04 02 20 sludges from on-site effluent treatment other than those mentioned in 04 02 19
- 04 02 21 wastes from unprocessed textile fibres
- 04 02 22 wastes from processed textile fibres
- 04 02 99 wastes not otherwise specified

# 05 WASTES FROM PETROLEUM REFINING, NATURAL GAS PURIFICATION AND PYROLYTIC TREATMENT OF COAL

### 05 01 wastes from petroleum refining

- 05 01 02\* desalter sludges
- 05 01 03\* tank bottom sludges
- 05 01 04\* acid alkyl sludges
- 05 01 05\* oil spills
- 05 01 06\* oily sludges from maintenance operations of the plant or equipment
- *05 01 07*\* acid tars
- 05 01 08\* other tars
- 05 01 09\*sludges from on-site effluent treatment containing dangerous substances05 01 10sludges from on-site effluent treatment other than those mentioned in 05
- 01 09
- 05 01 11\* wastes from cleaning of fuels with bases
- 05 01 12\* oil containing acids
- 05 01 13 boiler feedwater sludges
- 05 01 14 wastes from cooling columns
- 05 01 15\* spent filter clays
- *05 01 16* sulfur-containing wastes from petroleum desulphurisation
- 05 01 17 bitumen
- 05 01 99 wastes not otherwise specified

### 05 06 waste from the pyrolytic treatment of coal

- 05 06 01\* acid tars
- 05 06 03\* other tars
- 05 06 04 waste from cooling columns
- 05 06 99 wastes not otherwise specified

### 05 07 waste from natural gas purification and transportation

- 05 07 01\* wastes containing mercury
- 05 07 02 wastes containing sulfur
- 05 07 99 wastes not otherwise specified

### 06 WASTES FROM INORGANIC CHEMICAL PROCESSES

# 06 01 wastes from the manufacture, formulation, supply and use (MFSU) of acids

- 06 01 01\* sulfuric acid and sulfurous acid
- *06 01 02*\* hydrochloric acid
- 06 01 03\* hydrofluoric acid
- *06 01 04*\* phosphoric and phosphorous acid
- 06 01 05\* nitric acid and nitrous acid
- *06 01 06*\* other acids
- *06 01 99* wastes not otherwise specified

### 06 02 wastes from the MFSU of bases

06 02 01\* calcium hydroxide

- 06 02 03\* ammonium hydroxide
- 06 02 04\* sodium and potassium hydroxide 06 02 05\* other bases
- 06 02 99 wastes not otherwise specified

### 06 03 wastes from the MFSU of salts and their solutions and metallic oxides

- *06 03 11\** solid salts and solutions containing cyanides
- 06 03 13\* solid salts and solutions containing heavy metals
- 06 03 14 solid salts and solution other than those mentioned in 06 03 11 and 06 03 13
- 06 03 15\* metallic oxides containing heavy metals
- 06 03 16 metallic oxides other than those mentioned in 06 03 15
- 06 03 99 wastes not otherwise specified

### 06 04 metal-containing wastes other than those mentioned in 06 03

- 06 04 03\* wastes containing arsenic
- 06 04 04\* wastes containing mercury
- 06 04 05\* wastes containing other heavy metals
- 06 04 99 wastes not otherwise specified

## 06 05 sludges from on-site effluent treatment

06 05 02*	sludges from on-site effluent treatment containing dangerous solutions
06 05 03	sludges from onsite effluent treatment other than those mentioned in 06
	05 02

# 06 06 wastes from the MFSU of sulfur chemicals, sulfur chemical processes and desulphurisation processes

- 06 06 02\* wastes containing dangerous sulfides
- 06 06 03 wastes containing sulfides other than those mentioned in 06 06 02
- 06 06 99 wastes not otherwise specified

### 06 07 wastes from the MFSU of halogens and halogen chemical processes

- 06 07 01\* wastes containing asbestos from electrolysis
- *06 07 02\** activated carbon from chlorine production
- 06 07 03\* barium sulfate sludge containing mercury
- 06 07 04\* solutions and acids, for example contact acid
- 06 07 99 wastes not otherwise specified

### 06 08 wastes from the MFSU of silicon and silicon derivatives

- 06 08 02\* waste containing dangerous silicones
- 06 08 99 wastes not otherwise specified
- 06 10 wastes from the MFSU of nitrogen chemicals, nitrogen chemical processes and fertilizer manufacture
- 06 10 02\* wastes containing dangerous substances
- 06 10 99 wastes not otherwise specified

### 06 11 wastes from the manufacture of inorganic pigments and opacificiers

- 06 11 01 calcium-based reaction wastes from titanium dioxide production
- 06 11 99 wastes not otherwise specified
- 06 13 wastes from inorganic chemical processes not otherwise specified
- *06 13 01\** inorganic plant protection products, wood-preserving agents and other biocides
- 06 13 02\* spent activated carbon (except 06 07 02)
- 06 13 03 carbon black
- 06 13 04\* wastes from asbestos processing
- *06 13 05\** soot
- 06 13 99 wastes not otherwise specified

# 07 WASTES FROM ORGANIC CHEMICAL PROCESSES

# 07 01 wastes from the manufacture, formulation, supply and use (MFSU) of basic organic chemicals

- 07 01 01\* aqueous washing liquids and mother liquors
- 07 01 03\* organic halogenated solvents, washing liquids and mother liquors
- 07 01 04\* other organic solvents, washing liquids and mother liquors
- 07 01 07\* halogenated still bottoms and reaction residues
- 07 01 08\* other still bottoms and reaction residues
- 07 01 09\* halogenated filter cakes and spent absorbents
- 07 01 10\* other filter cakes and spent absorbents
- 07 01 11\* sludges from on-site effluent treatment containing dangerous substances
- 07 01 12 sludges from on-site effluent treatment other than those mentioned in 07 01 11
- 07 01 99 wastes not otherwise specified

#### 07 02 wastes from the MFSU of plastics, synthetic rubber and man-made fibres

- 07 02 01\* aqueous washing liquids and mother liquors
- 07 02 03\* organic halogenated solvents, washing liquids and mother liquors
- 07 02 04\* other organic solvents, washing liquids and mother liquors
- 07 02 07\* halogenated still bottoms and reaction residues
- 07 02 08\* other still bottoms and reaction residues
- 07 02 09\* halogenated filter cakes and spent absorbents
- 07 02 10\* other filter cakes and spent absorbents
- 07 02 11\* sludges from on-site effluent treatment containing dangerous substances
- 07 02 12 sludges from on-site effluent treatment other than those mentioned in 07 02 11
- 07 02 13 waste plastic
- 07 02 14\* wastes from additives containing dangerous substances

- 07 02 15 wastes from additives other than those mentioned in 07 02 14
- 07 02 16\* waste containing dangerous silicones
- 07 02 17 waste containing silicones other than those mentioned in 07 02 16
- 07 02 99 wastes not otherwise specified

# 07 03 wastes from the MFSU of organic dyes and pigments (except 06 11)

- 07 03 01\* aqueous washing liquids and mother liquors
- 07 03 03\* organic halogenated solvents, washing liquids and mother liquors
- 07 03 04\* other organic solvents, washing liquids and mother liquors
- 07 03 07\* halogenated still bottoms and reaction residues
- 07 03 08\* other still bottoms and reaction residues
- 07 03 09\* halogenated filter cakes and spent absorbent
- 07 03 10\* other filter cakes and spent absorbents
- 07 03 11\* sludges from on-site effluent treatment containing dangerous substances
- 07 03 12 sludges from on-site effluent treatment other than those mentioned in 07
- 03 11
- 07 03 99 wastes not otherwise specified

# 07 04 wastes from the MFSU of organic plant protection products (except 02 01 08 and 02 01 09), wood preserving agents (except 03 02) and other biocides

- 07 04 01\* aqueous washing liquids and mother liquors
- 07 04 03\* organic halogenated solvents, washing liquids and mother liquors
- 07 04 04\* other organic solvents, washing liquids and mother liquids
- 07 04 07\* halogenated still bottoms and reaction residues
- 07 04 08\* other still bottoms and reaction residues
- 07 04 09\* halogenated filter cakes and spent absorbents
- 07 04 10\* other filter cakes and spent absorbents
- 07 04 11\* sludges from on-site effluent treatment containing dangerous substances
- 07 04 12 sludges from on-site effluent treatment other than those mentioned in 07 04 11
- 07 04 13\* solid wastes containing dangerous substances
- 07 04 99 wastes not otherwise specified

#### 07 05 wastes from the MFSU of pharmaceuticals

- 07 05 01\* aqueous washing liquids and mother liquors
- 07 05 03\* organic halogenated solvents, washing liquids and mother liquors
- 07 05 04\* other organic solvents, washing liquids and mother liquors
- 07 05 07\* halogenated still bottoms and reaction residues

07 05 08\* other still bottoms and reaction residues 07 05 09\* halogenated filter cakes and spent absorbents

- 07 05 10\* other filter cakes and spent absorbents
- 07 05 11\* sludges from on-site effluent treatment containing dangerous substances
- 07 05 12 sludges from on-site effluent treatment other than those mentioned in 07
- 05 11
- 07 05 13\* solid wastes containing dangerous substances
- 07 05 14 solid wastes other than those mentioned in 07 05 13
- 07 05 99 wastes not otherwise specified

- 07 06 wastes from the MFSU of fats, grease, soaps, detergents, disinfectants and cosmetics
- 07 06 01\* aqueous washing liquids and mother liquors
- 07 06 03\* organic halogenated solvents, washing liquids and mother liquors
- 07 06 04\* other organic solvents, washing liquids and mother liquors
- 07 06 07\* halogenated still bottoms and reaction residues
- 07 06 08\* other sill bottoms and reaction residues
- 07 06 09\* halogenated filter cakes and spent absorbents
- 07 06 10\* other filter cakes and spent absorbents
- 07 06 11\* sludges from on-site effluent treatment containing dangerous substances
- 07 06 12 sludges from on-site effluent treatment other than those mentioned in 07 06 11
- 07 06 99 wastes not otherwise specified

# 07 07 wastes from the MFSU of fine chemicals and chemical products not otherwise specified

- 07 07 01\* aqueous washing liquids and mother liquors
- 07 07 03\* organic halogenated solvents, washing liquids and mother liquors
- 07 07 04\* other organic solvents, washing liquids and mother liquors
- 07 07 07\* halogenated still bottoms and reaction residues
- 07 07 08\* other still bottoms and reaction residues
- 07 07 09\* halogenated filter cakes and spent absorbents
- 07 07 10\* other filter cakes and spent absorbents
- 07 07 11\* sludges from on-site effluent treatment containing dangerous substances
- 07 07 12 sludges from on-site effluent treatment other than those mentioned in 07 07 11
- 07 07 99 wastes not otherwise specified

# 08 WASTES FORM THE MANUFACTURE, FORMULATION, SUPPLY AND USE (MFSU) OF COATINGS (PAINTS, VARNISHES AND VITREOUS ENAMELS,) ADHESIVES, SEALANTS AND PRINTING INKS

- 08 01 wastes from MFSU and removal of paint and varnish
- 08 01 11\* waste paint and varnish containing organic solvents or other dangerous substances
- 08 01 12 waste paint and varnish other than those mentioned in 08 01 11
- 08 01 13\* sludges from paint or varnish containing organic solvents or other dangerous substances
- 08 01 14 sludges from paint or varnish other than those mentioned in 08 01 13
- 08 01 15\* aqueous sludges containing paint or varnish containing organic solvents or other dangerous substances
- 08 01 16 aqueous sludges containing paint or varnish other than those mentioned in 08 01 15
- 08 01 17\* wastes from paint or varnish removal containing organic solvents or other dangerous substances
- 08 01 18 wastes from paint or varnish removal other than those mentioned in 08 01 17

- 08 01 19\* aqueous suspensions containing paint or varnish containing organic solvents or other dangerous substances
- 08 01 20 aqueous suspensions containing paint or varnish other than those montioned in 08 01 10
- mentioned in 08 01 19
- 08 01 21\* waste paint or varnish remover
- 08 01 99 wastes not otherwise specified
- 08 02 wastes from MFSU of other coatings (including ceramic materials)
- 08 02 01 waste coating powders
- 08 02 02 aqueous sludges containing ceramic materials
- 08 02 03 aqueous suspensions containing ceramic materials
- 08 02 99 wastes not otherwise specified

# 08 03 wastes from MFSU of printing inks

- 08 03 07 aqueous sludges containing ink
- 08 03 08 aqueous liquid waste containing ink
- 08 03 12\* waste ink containing dangerous substances
- 08 03 13 waste ink other than those mentioned in 08 03 12
- 08 03 14\* ink sludges containing dangerous substances
- 08 03 15 ink sludges other than those mentioned in 08 03 14
- 08 03 16\* waste etching solutions
- 08 03 17\* waste printing toner containing dangerous substances
- 08 03 18 waste printing toner other than those mentioned in 08 03 17
- *08 03 19*\* disperse oil
- 08 03 99 wastes not otherwise specified

# 08 04 wastes from MFSU of adhesives and sealants (including waterproofing products)

08 04 09\* waste adhesives and sealants containing organic solvents or other dangerous substances 08 04 10 waste adhesives and sealants other than those mentioned in 08 04 09 08 04 11\* adhesive and sealant sludges containing organic solvents or other dangerous substances 08 04 12 adhesive and sealant sludges other than those mentioned in 08 04 11 08 04 13\* aqueous sludges containing adhesives or sealants containing organic solvents or other dangerous substances 08 04 14 aqueous sludges containing adhesives or sealants other than those mentioned in 08 04 13 08 04 15\* aqueous liquid waste containing adhesives or sealants containing organic solvents or other dangerous substances 08 04 16 aqueous liquid waste containing adhesives or sealants other than those mentioned in 08 04 15 08 04 17\* rosin oil 08 04 99 wastes not otherwise specified

# 08 05 wastes not otherwise specified in 08

08 05 01\* waste isocyanates

# 09 WASTES FROM THE PHOTOGRAPHIC INDUSTRY

# 09 01 wastes for the photographic industry

- 09 01 01\* water-based developer and activator solutions
- 09 01 02\* water-based offset plate developer solutions
- 09 01 03\* solvent-based developer solutions
- 09 01 04\* fixed solutions
- 09 01 05\* bleach solutions and bleach fixer solutions
- 09 01 06\* wastes containing silver from on-site treatment of photographic wastes
- 09 01 07 photographic film and paper containing silver or silver compounds
- 09 01 08 photographic film and paper free of silver or silver compounds
- 09 01 10 single-use cameras without batteries
- 09 01 11\* single-use cameras containing batteries included in 16 06 01, 16 06 02 or 16 06 03
- 09 01 12 single-use cameras containing batteries other than those mentioned in 09 01 11
- 09 01 13\* aqueous liquid waste from on-site reclamation of silver other than those mentioned in 09 01 06
- 09 01 99 wastes not otherwise specified

### 10 WASTES FROM THERMAL PROCESSES

#### 10 01 wastes from power stations and other combustion plants (except 19)

10 01 01	bottom ash, slag and boiler dust (excluding boiler dust mentioned in 10
	01 04)
10 01 02	coal fly ash
10 01 03	fly ash from peat and untreated wood
10 01 04*	oil fly ash and boiler dust
10 01 05	calcium-based reaction wastes from flue-gas desulphurisation in solid
	form
10 01 07	calcium-based reaction wastes from flue-gas desulphurisation in sludge
	form
10 01 09*	sulfuric acid
10 01 13*	fly ash from emulsified hydrocarbons used as fuel
10 01 14*	bottom ash, slag and boiler dust from co-incineration containing
	dangerous substances
10 01 15	bottom ash, slag and boiler dust from co-incineration other than those
	mentioned in 10 01 14
10 01 16*	fly ash from co-incineration containing dangerous substances
10 01 17	fly ash from co-incineration other than those mentioned in 10 01 16
10 01 18*	wastes from gas cleaning containing dangerous substances
10 01 19	wastes from gas cleaning other than those mentioned in 10 01 05, 10 01
	07 and 10 01 18
10 01 20*	sludges from on-site effluent treatment containing dangerous substances
10 01 21	sludges from on-site effluent treatment other than those mentioned in 10
	01 20
10 01 22*	aqueous sludges from boiler cleansing containing dangerous substances

- *10 01 23* aqueous sludges from boiler cleansing other than those mentioned in *10 01 22*
- *10 01 24* sands from fluidized beds
- *10 01 25* wastes from fuel storage and preparation of coal-fired power plants
- *10 01 26* wastes from cooling-water treatment
- *10 01 99* wastes not otherwise specified

#### 10 02 wastes from the iron and steel industry

- *10 02 01* wastes from the processing of slag
- 10 02 02 unprocessed slag
- *10 02 07\** solid wastes from gas treatment containing dangerous substances
- 10 02 08 solid wastes from gas treatment other than those mentioned in 10 02 07
- *10 02 10* mill scales
- *10 02 11\** wastes from cooling-water treatment containing oil
- *10 02 12* waste from cooling-water treatment other than those mentioned in *10 02 11*
- *10 02 13\** sludges and filter cakes from gas treatment containing dangerous substances
- 10 02 14 sludges and filter cakes from gas treatment other than those mentioned in 10 02 13
- *10 02 15* other sludges and filter cakes
- 10 02 99 wastes not otherwise specified

#### 10 03 wastes from aluminum thermal metallurgy

- *10 03 02* anode scraps
- *10 03 04\** primary production slags
- 10 03 05 waste alumina
- *10 03 08*\* salt slags from secondary production
- *10 03 09\** black drosses from secondary production
- *10 03 15\** skimmings that are flammable or emit, upon contact with water,

flammable gases in dangerous quantities

- *10 03 16* skimming other than those mentioned in *10 03 15*
- *10 03 17\** tar-containing wastes from anode manufacture
- *10 03 18* carbon-containing wastes from anode manufacture other than those mentioned in *10 03 17*
- *10 03 19\** flue-gas dust containing dangerous substances
- 10 03 20 flue-gas dust other than those mentioned in 10 03 19
- *10 03 21\** other particulates and dust (including ball-mill dust) containing

dangerous substances

*10 03 22* other particulates and dust (including ball-mill dust) other than those mentioned in *10 03 21* 

- *10 03 23\** solid wastes from gas treatment containing dangerous substances
- 10 03 24 solid wastes from gas treatment other than those mentioned in 10 03 23
- *10 03 25\** sludges and filter cakes from gas treatment containing dangerous substances
- *10 03 26* sludges and filter cakes from gas treatment other than those mentioned in *10 03 25*
- *10 03 27\** wastes from cooling-water treatment containing oil

10 03 28	wastes from cooling-water treatment other than those mentioned in <i>10</i> 03 27		
10 03 29*	waste from treatment of salt slags and black drosses containing		
	dangerous substances		
10 03 30	wastes from treatment of salt slags and black drosses other than those		
10.02.00	mentioned in 10 03 29		
10 03 99	wastes not otherwise specified		
	from lead thermal metallurgy		
10 04 01*	slags from primary and secondary production		
10 04 02*	dross and skimmings from primary and secondary production		
10 04 03*	calcium arsenate		
10 04 04*	flue-gas dust		
10 04 05*	other particulates and dust		
10 04 06*	solid wastes from gas treatment		
10 04 07*	sludges and filter cakes from gas treatment		
10 04 09*	wastes from cooling-water treatment containing oil		
10 04 10	waste from cooling-water treatment other than those mentioned in 10 04		
	09		
10 04 99	wastes not otherwise specified		
	10 05 wastes from zinc thermal metallurgy		
10 05 01	slags from primary and secondary production		
10 05 03*	flue-gas dust		
10 05 04	other particulates and dust		
10 05 05*	solid waste from gas treatment		
10 05 06*	sludges and filter cakes from gas treatment		
10 05 08*	wastes from cooling-water treatment containing oil		
10 05 09	wastes from cooling-water treatment other than those mentioned in <i>10</i> 05 08		
10 05 10*	dross and skimmings that are flammable or emit, upon contact with		
	water, flammable gases in dangerous quantities		
10 05 11	dross and skimmings other than those mentioned in 10 05 10		
10 05 99	wastes not otherwise specified		
10 06 wastes	from copper thermal metallurgy		
10 06 01	slags from primary and secondary production		
10 06 02	dross and skimmings from primary and secondary production		
10 06 03*	flue-gas dust		
10 06 04	other particulates and dust		
10 06 06*	solid wastes from gas treatment		
10 06 07*	sludges and filter cakes from has treatment		
10 06 09*	wastes from cooling-water treatment containing oil		
10 06 10	waste from cooling-water treatment other than those mentioned in 10 06		
	09		
10 06 99	wastes not otherwise specified		

10 07 wastes from silver, gold and platinum thermal metallurgy

10 07 01	slags from primary and secondary production
10 07 02	dross and skimmings from primary and secondary production
10 07 03	solid wastes from gas treatment
10 07 04	other particultes and dust
10 07 05	sludges and filter cakes from gas treatment
10 07 07*	wastes from cooling-water treatment containing oil
10 07 08	wastes from cooling-water treatment other than those mentioned in 10
10.07.00	07 07
10 07 99	wastes not otherwise specified
	from other non-ferrous thermal metallurgy
10 08 04	particulates and dust
10 08 08*	salt slag from primary and secondary production
10 08 09	other slags
10 08 10*	dross and skimming that are flammable or emit, upon the contact with
	water, flammable gases in dangerous quantities
10 08 11	dross and skimmings other than those mentioned in 10 08 10
10 08 12*	tar-containing waste from anode manufacture
10 08 13	carbon-containing wastes from anode manufacture other than those mentioned in <i>10 08 12</i>
10 08 14	anode scrap
10 08 15*	flue-gas dust containing dangerous substances
10 08 16	flue-gas dust other than those mentioned in 10 08 15
10 08 17*	sludges and filter cakes from flue-gas treatment containing dangerous substances
10 08 18	sludges and filter cakes from flue-gas treatment other than those
10 00 10	mentioned in 10 08 17
10 08 19*	wastes from cooling-water treatment containing oil
10 08 20	wastes from cooling-water treatment other than those mentioned in <i>10</i> 08 19
10 08 99	wastes not otherwise specified
10 09 wastes	from casting of ferrous pieces
10 09 03	furnace slag
10 09 05*	casting cores and moulds which have not undergone pouring containing
	dangerous substances
10 09 06	casting cores and moulds which have not undergone pouring other than those mentioned in <i>10 09 05</i>
10 09 07*	casting cores and moulds which have undergone pouring containing

- dangerous substances 10 09 08 casting cores and moulds have undergone pouring other than those
- *10 09 08* casting cores and moulds have undergone pouring other that mentioned in *10 09 07*
- *10 09 09\** flue-gas dust containing dangerous substances
- 10 09 10 flue-gas dust other than those mentioned in 10 09 09
- *10 09 11\** other particulates containing dangerous substances
- 10 09 12 other particulates other than those mentioned in 10 09 11
- *10 09 13\** waste binders containing dangerous substances

- *10 09 14* waste binders other than those mentioned in *10 09 13*
- *10 09 15\** waste crack-indicating agent containing dangerous substances
- 10 09 16 waste crack-indicating agent other than those mentioned in 10 09 15
- 10 09 99 wastes not otherwise specified

# 10 10 wastes from casting of non-ferrous pieces

- *10 10 03* furnace slag
- *10 10 05\** casting cores and moulds which have not undergone pouring, containing dangerous substances
- 10 10 06 casting cores and moulds which have not undergone pouring, other than those mentioned in 10 10 05
- *10 10 07\** casting cores and moulds which have undergone pouring, containing dangerous substances
- 10 10 08 casting cores and moulds which have undergone pouring, other than those mentioned in 10 10 07
- *10 10 09\** flue-gas dust containing dangerous substances
- 10 10 10 flue-gas dust other than those mentioned in 10 10 09
- 10 10 11\* other particulates containing dangerous substances
- 10 10 12 other particulates other than those mentioned in 10 10 11
- 10 10 13\* waste binders containing dangerous substances
- 10 10 14 waste binders other than those mentioned in 10 10 13
- *10 10 15\** waste crack-indicating agent containing dangerous substances
- 10 10 16 waste crack-indicating agent other than those mentioned in 10 10 15
- *10 10 99* wastes not otherwise specified

#### 10 11 wastes from manufacture of glass and glass products

- *10 11 03* waste glass-based fibrous materials
- *10 11 05* particulates and dust
- *10 11 09\** waste preparation mixture before thermal processing, containing dangerous substances
- *10 11 10* waste preparation mixture before thermal processing, other than those mentioned in *10 11 09*
- *10 11 11\** waste glass in small particles and glass powder containing heavy metals (for example from cathode ray tubes)
- *10 11 12* waste glass other than those mentioned in *10 11 11*
- 10 11 13\* glass-polishing and -grinding sludge containing dangerous substances
- *10 11 14* glass-polishing and -grinding sludge other than those mentioned in *10*
- 11 13
- 10 11 15\* solid wastes from flue-gas treatment containing dangerous substances
- 10 11 16 solid wastes from flue-gas treatment other than those mentioned in 10 11 15
- *10 11 17\** sludges and filter cakes from flue-gas treatment containing dangerous substances
- *10 11 18* sludges and filter cakes from flue-gas treatment other than those mentioned in *10 11 17*
- *10 11 19\** solid wastes from on-site effluent treatment containing dangerous substances

- *10 11 20* solid wastes from on-site effluent treatment other than those mentioned in *10 11 19*
- 10 11 99 wastes not otherwise specified

# 10 12 wastes from manufacture of ceramic goods, bricks, tiles and construction products

- *10 12 01* waste preparation mixture before thermal processing
- *10 12 03* particulates and dust
- *10 12 05* sludges and filter cakes from gas treatment
- 10 12 06 discarded moulds
- *10 12 08* waste ceramics, bricks, tiles and construction products (after thermal processing)
- 10 12 09\* solid wastes from gas treatment containing dangerous substances
- 10 12 10 solid wastes from gas treatment other than those mentioned in 10 12 09
- *10 12 11\** wastes from glazing containing heavy metals
- *10 12 12* wastes from glazing other than those mentioned in *10 12 11*
- *10 12 13* sludge from on-site effluent treatment
- 10 12 99 wastes not otherwise specified

# 10 13 wastes from manufacture of cement, lime and plaster and articles and products made from them

- *10 13 01* waste preparation mixture before thermal processing
- *10 13 04* wastes from calcination and hydration of lime
- 10 13 06 particulates and dust (except 10 13 12 and 10 13 13)
- *10 13 07* sludges and filter cakes from gas treatment
- *10 13 09\** wastes from asbestos-cement manufacture containing asbestos
- *10 13 10* wastes from asbestos-cement manufacture other than those mentioned in *10 13 09*
- *10 13 11* wastes from cement-based composite materials other than those mentioned in *10 13 09* and *10 13 10*
- *10 13 12\** solid wastes from gas treatment containing dangerous substances
- *10 13 13* solid wastes from gas treatment other than those mentioned in *10 13 12*
- *10 13 14* waste concrete and concrete sludge
- 10 13 99 wastes not otherwise specified

# 10 14 waste from crematoria

10 14 01\* waste from gas cleaning containing mercury

# 11 WASTES FROM CHEMICAL SURFACE TREATMENT AND COATING OF METALS AND OTHER MATERIALS; NON-FERROUS HYDRO-METALLURGY

- 11 01 wastes from chemical surface treatment and coating of metals and other materials (for example galvanic processes, zinc coating processes, pickling processes, etching, phosphating, alkaline degreasing, anodizing)
- 11 01 05\* pickling acids
- 11 01 06\* acids not otherwise specified
- 11 01 07\* pickling bases

- *11 01 08*\* phosphatising sludges
- *11 01 09*\* sludges and filter cakes containing dangerous substances
- 11 01 10 sludges and filter cakes other than those mentioned in 11 01 09
- 11 01 11\* aqueous rinsing liquids containing dangerous substances
- *11 01 12* aqueous rinsing liquids other than those mentioned in *11 01 11*
- 11 01 13\* degreasing wastes containing dangerous substances
- *11 01 14* degreasing wastes other than those mentioned in *11 01 13*
- *11 01 15\** eluate and sludges from membrane systems or ion exchange systems containing dangerous substances
- 11 01 16\* saturated or spent ion exchange resins
- 11 01 98\* other wastes containing dangerous substances
- *11 01 99* wastes not otherwise specified

#### 11 02 waste from non-ferrous hydrometallurgical processes

11 02 02*	sludges from zinc hydrometallurgy (including jarosite, goethite)
11 02 03	wastes from the production of anodes for aqueous electrolytical
	processes
11 02 05*	wastes from copper hydrometallurgical processes containing dangerous
	substances
11 02 06	wastes from copper hydrometallurgical processes other than those
	mentioned in 11 02 05
11 02 07*	other wastes containing dangerous substances
11 02 99	wastes not otherwise specified

#### 11 03 sludges and solids from tempering processes

- 11 03 01\* waste containing cyanide
- 11 03 02\* other wastes

#### 11 05 wastes from hot galvanizing processes

- *11 05 01* hard zinc
- *11 05 02* zinc ash
- 11 05 03\* solid wastes from gas treatment
- *11 05 04*\* spent flux
- *11 05 99* wastes not otherwise specified

### 12 WASTES FROM SHAPING AND PHYSICAL AND MECHANICAL SURFACE TREATMENT OF METALS AND PLASTICS

# 12 01 wastes from shaping and physical and mechanical surface treatment of metals and plastics

- *12 01 01* ferrous metal filings and turnings
- *12 01 02* ferrous metal dust and particles
- *12 01 03* non-ferrous metal filings and turnings
- *12 01 04* non-ferrous metal dust and particles
- *12 01 05* plastics shavings and turnings
- *12 01 06\** mineral-based machining oils containing halogens (except emulsions and solutions)

- 12 01 07\* mineral-based machining oils free of halogens (except emulsions and
- solutions)
- 12 01 08\* machining emulsions and solutions containing halogens
- 12 01 09\* machining emulsions and solutions free of halogens
- *12 01 10*\* synthetic machining oils
- 12 01 12\* spent waxes and fats
- 12 01 13 welding wastes
- *12 01 14\** machining sludges containing dangerous substances
- *12 01 15* machining sludges other than those mentioned in *12 01 14*
- *12 01 16\** waste blasting material containing dangerous substances
- *12 01 17* waste blasting material other than those mentioned in 12 01 16
- 12 01 18\* metal sludge (grinding, honing and lapping sludge) containing oil
- *12 01 19\** readily biodegradable machining oil
- *12 01 20\** spent grinding bodies and grinding materials containing dangerous substances
- *12 01 21* spent grinding bodies and grinding materials other than those mentioned in *12 01 20*
- *12 01 99* wastes not otherwise specified

# 12 03 wastes from water and steam degreasing processes (except 11)

- 12 03 01\* aqueous washing liquids
- 12 03 02\* steam degreasing wastes

# 13 OIL WASTES AND WASTES OF LIQUID FUELS (except edible oils, and those in chapters 05, 12 and 19)

#### 13 01 waste hydraulic oils

- *13 01 01*\* hydraulic oils, containing PCBs (15)
- *13 01 04*\* chlorinated emulsions
- *13 01 05*\* non-chlorinated emulsions
- 13 01 09\* mineral-based chlorinated hydraulic oils
- 13 01 10\* mineral-based non-chlorinated hydraulic oils
- 13 01 11\* synthetic hydraulic oils
- *13 01 12\** readily biodegradable hydraulic oils
- *13 01 13*\* other hydraulic oils

#### 13 02 waste engine, gear and lubricating oils

- *13 02 04\** mineral-based chlorinated engine, gear and lubricating oils
- 13 02 05\* mineral-based non-chlorinated engine, gear and lubricating oils
- *13 02 06*\* synthetic engine, gear and lubricating oils
- 13 02 07\* readily biodegradable engine, gear and lubricating oils
- 13 02 08\* other engine, gear and lubricating oils

#### 13 03 waste insulating and heat transmission oils

- 13 03 01\* insulating or heat transmission oils containing PCBs
- 13 03 06\* mineral-based chlorinated insulating and heat transmission oils other than those mentioned in 13 03 01
- 13 03 07\* mineral-based non-chlorinated insulating and heat transmission oils

- *13 03 08*\* synthetic insulating and heat transmission oils
- 13 03 09\* readily biodegradable insulating and heat transmission oils
- 13 03 10\* other insulating and heat transmission oils

# 13 04 bilge oils

- *13 04 01*\* bilge oils from inland navigation
- *13 04 02\** bilge oils from jetty sewers
- *13 04 03*\* bilge oils from other navigation

# 13 05 oil/water separator contents

- 13 05 01\* solids from grit chambers and oil/water separators
- 13 05 02\* sludges from oil/water separators
- 13 05 03\* interceptor sludges
- *13 05 06*\* oil from oil/water separators
- *13 05 07\** oily water from oil/water separators
- 13 05 08\* mixtures of wastes from grit chambers and oil/water separators

# 13 07 wastes of liquid fuels

- 13 07 01\* fuel oil and diesel
- *13 07 02*\* petrol
- *13 07 03\** other fuels (including mixtures)

# 13 08 oil wastes not otherwise specified

- *13 08 01*\* desalter sludges or emulsions
- 13 08 02\* other emulsions
- 13 08 99\* wastes not otherwise specified

# 14 WASTE ORGANIC SOLVENTS, REFRIGERANTS AND PROPELLANTS (except 07 and 08)

#### 14 06 waste organic solvents, refrigerants and foam/aerosol propellants

- 14 06 01\* chlorofluorocarbons, HCFC, HFC
- 14 06 02\* other halogenated solvents and solvent mixtures
- 14 06 03\* other solvents and solvent mixtures
- 14 06 04\* sludges or solid wastes containing halogenated solvents
- 14 06 05\* sludges or solid wastes containing other solvents

# 15 WASTE PACKAGING; ABSORBENTS, WIPING CLOTHS, FILTER MATERIALS AND PROTECTIVE CLOTHING NOT OTHERWISE SPECIFIED

### 15 01 packaging (including separately collected municipal packaging waste)

- 15 01 01 paper and cardboard packaging
- 15 01 02 plastic packaging
- 15 01 03 wooden packaging
- *15 01 04* metallic packaging
- 15 01 05 composite packaging

- 15 01 06 mixed packaging
- *15 01 07* glass packaging
- *15 01 09* textile packaging
- *15 01 10\** packaging containing residues of or contaminated by dangerous substances
- *15 01 11\** metallic packaging containing a dangerous solid porous matrix (for example asbestos), including empty pressure containers

#### 15 02 absorbents, filter materials, wiping cloths and protective clothing

- 15 02 02\* absorbents, filter materials (including oil filters not otherwise specified), wiping cloths, protective clothing contaminated by dangerous substances
- *15 02 03* absorbents, filter materials, wiping cloths and protective clothing other than those mentioned in *15 02 02*

# 16 WASTES NOT OTHERWISE SPECIFIED IN THE LIST

# 16 01 end-of-life vehicles from different means of transport (including off-road machinery) and wastes from dismantling of end-of-life vehicles and vehicle maintenance (except 13, 14, 16 06 and 16 08)

*16 01 03* end-of-life tyres

- *16 01 06* end-of-life vehicles, containing neither liquids nor other hazardous components
- *16 01 07*\* oil filters
- *16 01 08*\* components containing mercury
- *16 01 09*\* components containing PCBs
- *16 01 10\** explosive components (for example air bags)
- *16 01 11\** brake pads containing asbestos
- *16 01 12* brake pads other than those mentioned in *16 01 11*
- *16 01 13*\* brake fluids
- *16 01 14\** antifreeze fluids containing dangerous substances
- *16 01 15* antifreeze fluids other than those mentioned in *16 01 14*
- *16 01 16* tanks for liquefied gas
- *16 01 17* ferrous metal
- *16 01 18* non-ferrous metal
- *16 01 19* plastic
- 16 01 20 glass
- $16\ 01\ 21^*$  hazardous components other than those mentioned in 16 01 07 to 16 01
- 11 and 16 01 13 and 16 01 14
- *16 01 22* components not otherwise specified
- *16 01 99* wastes not otherwise specified

#### 16 02 wastes from electrical and electronic equipment

- *16 02 09\** transformers and capacitors containing PCBs
- *16 02 10\** discarded equipment containing or contaminated by PCBs other than those mentioned in *16 02 09*
- *16 02 11\** discarded equipment containing chlorofluorocarbons, HCFC, HFC

- *16 02 12\** discarded equipment containing free asbestos
- *16 02 13\** discarded equipment containing hazardous components (16) other than those mentioned in *16 02 09* to *16 02 12*
- *16 02 14* discarded equipment other than those mentioned in *16 02 09* to *16 02 13*
- *16 02 15\** hazardous components removed from discarded equipment
- *16 02 16* components removed from discarded equipment other than those
  - mentioned in 16 02 15

# 16 03 off-specification batches and unused products

- *16 03 03\** inorganic wastes containing dangerous substances
- *16 03 04* inorganic wastes other than those mentioned in *16 03 03*
- *16 03 05\** organic wastes containing dangerous substances
- *16 03 06* organic wastes other than those mentioned in *16 03 05*

# 16 04 waste explosives

- 16 04 01\* waste ammunition
- *16 04 02\** fireworks wastes
- *16 04 03\** other waste explosives

#### 16 05 gases in pressure containers and discarded chemicals

- *16 05 04\** gases in pressure containers (including halons) containing dangerous substances
- 16 05 05 gases in pressure containers other than those mentioned in 16 05 04
- *16 05 06\** laboratory chemicals, consisting of or containing dangerous substances, including mixtures of laboratory chemicals
- *16 05 07\** discarded inorganic chemicals consisting of or containing dangerous substances
- *16 05 08*\* discarded organic chemicals consisting of or containing dangerous substances
- *16 05 09* discarded chemicals other than those mentioned in *16 05 06*, *16 05 07* or *16 05 08*

# 16 06 batteries and accumulators

- 16 06 01\* lead batteries
- 16 06 02\* Ni-Cd batteries
- *16 06 03*\* mercury-containing batteries
- *16 06 04* alkaline batteries (except *16 06 03*)
- *16 06 05* other batteries and accumulators
- 16 06 06\* separately collected electrolyte from batteries and accumulators

# 16 07 wastes from transport tank, storage tank and barrel cleaning (except 05 and 13)

- *16 07 08*\* wastes containing oil
- *16 07 09\** wastes containing other dangerous substances
- *16 07 99* wastes not otherwise specified

- 16 08spent catalysts16 08 01spent catalysts containing gold, silver, rhenium, rhodium, palladium,<br/>iridium or platinum (except 16 08 07)
- *16 08 02\** spent catalysts containing dangerous transition metals or dangerous transition metal compounds
- *16 08 03* spent catalysts containing transition metals or transition metal compounds not otherwise specified
- 16 08 04 spent fluid catalytic cracking catalysts (except 16 08 07)
- *16 08 05\** spent catalysts containing phosphoric acid
- *16 08 06\** spent liquids used as catalysts
- *16 08 07\** spent catalysts contaminated with dangerous substances

# 16 09 oxidizing substances

- *16 09 01\** permanganates, for example potassium permanganate
- *16 09 02\** chromates, for example potassium chromate, potassium or sodium dichromate
- *16 09 03\** peroxides, for example hydrogen peroxide
- *16 09 04\** oxidizing substances, not otherwise specified

# 16 10 aqueous liquid wastes destined for off-site treatment

- 16 10 01\* aqueous liquid wastes containing dangerous substances
- *16 10 02* aqueous liquid wastes other than those mentioned in *16 10 01*
- *16 10 03\** aqueous concentrates containing dangerous substances
- *16 10 04* aqueous concentrates other than those mentioned in *16 10 03*

# 16 11 waste linings and refractories

- *16 11 01\** carbon-based linings and refractories from metallurgical processes containing dangerous substances
- *16 11 02* carbon-based linings and refractories from metallurgical processes other than those mentioned in *16 11 01*
- *16 11 03\** other linings and refractories from metallurgical processes containing dangerous substances
- 16 11 04 other linings and refractories from metallurgical processes other than those mentioned in 16 11 03
- *16 11 05\** linings and refractories from non-metallurgical processes containing dangerous substances
- *16 11 06* linings and refractories from non-metallurgical processes other than those mentioned in *16 11 05*

# 17 CONSTRUCTION AND DEMOLITION WASTES (INCLUDING EXCAVATED SOIL FROM CONTAMINATED SITES)

# 17 01 concrete, bricks, tiles and ceramics

- *17 01 01* concrete
- *17 01 02* bricks
- *17 01 03* tiles and ceramics
- 17 01 06\* mixtures of, or separate fractions of concrete, bricks, tiles and ceramics containing dangerous substances

*17 01 07* mixture of concrete, bricks, tiles and ceramics other than those mentioned in *17 01 06* 

# 17 02 wood, glass and plastic

- *17 02 01* wood
- 17 02 02 glass
- *17 02 03* plastic
- 17 02 04\* glass, plastic and wood containing or contaminated with dangerous substances

# 17 03 bituminous mixtures, coal tar and tarred products

- *17 03 01\** bituminous mixtures containing coal tar
- 17 03 02 bituminous mixtures containing other than those mentioned in 17 03 01
- *17 03 03*\* coal tar and tarred products

# 17 04 metals (including their alloys)

17 04 metals	(including their alloys)
17 04 01	copper, bronze, brass
17 04 02	aluminum
17 04 03	lead
17 04 04	zinc
17 04 05	iron and steel
17 04 06	tin
17 04 07	mixed metals
17 04 09*	metal waste contaminated with dangerous substances
17 04 10*	cables containing oil, coal tar and other dangerous substances
17 04 11	cables other than those mentioned in 17 04 10
17 05 soil (including excavated soil from contaminated sites), stones and dredging	
spoil	
17 05 03*	soil and stones containing dangerous substances
17 05 04	soil and stones other than those mentioned in 17 05 03
17 05 05*	dredging spoil containing dangerous substances
17 05 06	dredging spoil other than those mentioned 17 05 05
17 05 07*	track ballast containing dangerous substances
17 05 08	track ballast other than those mentioned in 17 05 07,
17 06 insulat	tion materials and asbestos-containing construction materials
17 06 01*	insulation materials containing asbestos
17 06 03*	other insulation materials consisting of or containing dangerous substances
17 06 04	insulation materials other than those mentioned in 17 06 01 and 17 06
	03
17 06 05*	construction materials containing asbestos
17 08 gypsum-based construction material	
17 08 01*	gypsum-based construction materials contaminated with dangerous substances
17 08 02	gypsum-based construction materials other than those mentioned in 17

*17 08 02* gypsum-based construction materials other than those mentioned in *17* 08 01

#### 17 09 other construction and demolition waste

- *17 09 01\** construction and demolition wastes containing mercury
- 17 09 02\* construction and demolition wastes containing PCB (for example PCBcontaining sealants, PCB-containing resin-based floorings, PCBcontaining sealed glazing units, PCB-containing capacitors)
- 17 09 03\* other construction and demolition wastes (including mixed wastes) containing dangerous substances
- 17 09 04 mixed construction and demolition wastes other than those mentioned in 17 09 01, 17 09 02 and 17 09 03

# 18 WASTES FROM HUMAN OR ANIMAL HEALTH CARE AND/OR RELATED RESEARCH (except kitchen and restaurant wastes not arising from immediate health care)

# 18 01 wastes from natal care, diagnosis, treatment or prevention of disease in humans

- 18 01 01 sharps (except 18 01 03)
- 18 01 02 body parts and organs including blood bags and blood preserves (except 18 01 03)
- 18 01 03\* wastes whose collection and disposal is subject to special requirements in order to prevent infection
- 18 01 04 wastes whose collection and disposal is not subject to special requirements in order to prevent infection (for example dressings, plaster casts, linen, disposable clothing, diapers)
- 18 01 06\* chemicals consisting of or containing dangerous substances
- 18 01 07 chemicals other than those mentioned in 18 01 06
- 18 01 08\* cytotoxic and cytostatic medicines
- 18 01 09 medicines other than those mentioned in 18 01 08
- 18 01 10\* amalgam waste from dental care

# 18 02 wastes from research, diagnosis, treatment or prevention of disease involving animals

18 02 01 sharps except (18 02 02) 18 02 02\* wastes whose collection and disposal is subject to special requirements in order to prevent infection wastes whose collection and disposal is not subject to special 18 02 03 requirements in order to prevent infection 18 02 05\* chemicals consisting of or containing dangerous substances 18 02 06 chemicals other than those mentioned in 18 02 05 18 02 07\* cytotoxic and cytostatic medicines medicines other than those mentioned in 18 02 07 18 02 08

# 19 WASTES FROM WASTE MANAGEMENT FACILITIES, OFF-SITE WASTE WATER TREATMENT PLANTS AND THE PREPARATION OF WATER INTENDED FOR HUMAN CONSUMPTION AND WATER FOR INDUSTRIAL USE

# 19 01 wastes from incineration or pyrolysis of waste

- *19 01 02* ferrous materials removed from bottom ash
- *19 01 05*\* filter cake from gas treatment
- *19 01 06\** aqueous liquid wastes from gas treatment and other aqueous liquid wastes
- *19 01 07\** solid wastes from gas treatment
- *19 01 10\** spent activated carbon from flue-gas treatment
- *19 01 11\** bottom ash and slag containing dangerous substances
- *19 01 12* bottom ash and slag other than those mentioned in *19 01 11*
- *19 01 13*\* fly ash containing dangerous substances
- 19 01 14 fly ash other than those mentioned in 19 01 13
- *19 01 15\** boiler dust containing dangerous substances
- *19 01 16* boiler dust other than those mentioned in *19 01 15*
- *19 01 17\** pyrolysis wastes containing dangerous substances
- *19 01 18* pyrolysis wastes other than those mentioned in *19 01 17*
- *19 01 19* sands from fluidized beds
- *19 01 99* wastes not otherwise specified

# 19 02 wastes from physico/chemical treatments of waste (including dechromatation, decyanidation, neutralization)

19 02 03 19 02 04*	premixed wastes composed only of non-hazardous wastes premixed wastes composed of at least one hazardous waste
19 02 05*	sludges from physico/chemical treatment containing dangerous
substances	
19 02 06	sludges from physico/chemical treatment other than those mentioned in 19 02 05
19 02 07*	oil and concentrates from separation
19 02 08*	liquid combustible wastes containing dangerous substances
19 02 09*	solid combustible wastes containing dangerous substances
19 02 10	combustible wastes other than those mentioned in $19\ 02\ 08$ and $19\ 02$
10 00 11*	
19 02 11*	other wastes containing dangerous substances
19 02 99	wastes not otherwise specified

#### 19 03 stabilized/solidified wastes

- 19 03 04\* wastes marked as hazardous, partly stabilized
- *19 03 05* stabilized wastes other than those mentioned in *19 03 04*
- 19 03 06\* wastes marked as hazardous, solidified
- *19 03 07* solidified wastes other than those mentioned in *19 03 06*

#### 19 04 vitrified waste and wastes from vitrification

- *19 04 01* vitrified waste
- 19 04 02\* fly ash and other flue-gas treatment wastes
- *19 04 03*\* non-vitrified solid phase
- *19 04 04* aqueous liquid wastes from vitrified waste tempering

#### 19 05 wastes from aerobic treatment of solid wastes

- *19 05 01* non-composted fraction of municipal and similar wastes
- *19 05 02* non-composted fraction of animal and vegetable waste
- *19 05 03* off-specification compost
- *19 05 99* wastes not otherwise specified

#### 19 06 wastes from anaerobic treatment of waste

- *19 06 03* liquor from anaerobic treatment of municipal waste
- *19 06 04* digestate from anaerobic treatment of municipal waste
- *19 06 05* liquor from anaerobic treatment of animal and vegetable waste
- *19 06 06* digestate from anaerobic treatment of animal and vegetable waste
- *19 06 99* wastes not otherwise specified

#### 19 07 landfill leachate

19 07 02* landfill leachate containing dangerous substances	19 07 02*	landfill leachate	containing dangerou	s substances
-------------------------------------------------------------	-----------	-------------------	---------------------	--------------

- *19 07 03* landfill leachate other than those mentioned in *19 07 02*
- 19 08 wastes from waste water treatment plants not otherwise specified
- 19 08 01 screenings
- *19 08 02* waste from desanding
- *19 08 05* sludges from treatment of urban waste water
- *19 08 06*\* saturated or spent ion exchange resins
- *19 08 07\** solutions and sludges from regeneration of ion exchangers
- *19 08 08*\* membrane system waste containing heavy metals
- *19 08 09* grease and oil mixture from oil/water separation containing only edible oil and fats
- *19 08 10\** grease and oil mixture from oil/water separation other than those mentioned in *19 08 09*
- *19 08 11\** sludges containing dangerous substances from biological treatment of Industrial waste water
- *19 08 12* sludges from biological treatment of industrial waste water other than those mentioned in *19 08 11*
- *19 08 13\** sludges containing dangerous substances from other treatment of industrial waste water
- *19 08 14* sludges from other treatment of industrial waste water other than those mentioned in *19 08 13*
- 19 08 99 wastes not otherwise specified

# *19 09 wastes from the preparation of water intended for human consumption or water for industrial use*

*19 09 01* solid waste from primary filtration and screenings

- sludges from water clarification 19 09 02
- 19 09 03 sludges from decarbonation
- 19 09 04 spent activated carbon
- 19 09 05 saturated or spent ion exchange resins
- 19 09 06 solutions and sludges from regeneration of ion exchangers
- 19 09 99 wastes not otherwise specified

### 19 10 wastes from shredding of metal-containing wastes

- 19 10 01 iron and steel waste
- 19 10 02 non-ferrous waste
- 19 10 03\* fluff-light fraction and dust containing dangerous substances
- 19 10 04 fluff-light fraction and dust other than those mentioned in 19 10 03
- 19 10 05\* other fractions containing dangerous substances
- 19 10 06 other fractions other than those mentioned in 19 10 05

# 19 11 wastes from oil regeneration

- 19 11 01\* spent filter clays
- 19 11 02\* acid tars
- 19 11 03\* aqueous liquid wastes
- 19 11 04\* wastes from cleaning of fuel with bases
- 19 11 05\* sludges from on-site effluent treatment containing dangerous substances sludges from on-site effluent treatment other than those mentioned in 19
- 19 11 06
- 11 05
- 19 11 07\* wastes from flue-gas cleaning
- 19 11 99 wastes not otherwise specified

# 19 12 wastes from the mechanical treatment of waste (for example sorting, crushing, compacting, palletizing) not otherwise specified

- 19 12 01 paper and cardboard
- 19 12 02 ferrous metal
- 19 12 03 non-ferrous metal
- plastic and rubber 19 12 04
- 19 12 05 glass
- 19 12 06\* wood containing dangerous substances
- 19 12 07 wood other than that mentioned in 19 12 06
- 19 12 08 textiles
- 19 12 09 minerals (for example sand, stones)
- 19 12 10 combustible waste (refuse derived fuel)
- 19 12 11\* other wastes (including mixtures of materials) from mechanical treatment of waste containing dangerous substances
- 19 12 12 other wastes (including mixtures of materials) from mechanical treatment of wastes other than those mentioned in 19 12 11

#### 19 13 wastes from soil and groundwater remediation

- 19 13 01\* solid wastes from soil remediation containing dangerous substances
- 19 13 02 solid wastes from soil remediation other than those mentioned in 1913 01
- 19 13 03\* sludges from soil remediation containing dangerous substances

- *19 13 04* sludges from soil remediation other than those mentioned in *19 13 03*
- *19 13 05\** sludges from groundwater remediation containing dangerous substances
- *19 13 06* sludges from groundwater remediation other than those mentioned in *19 13 05*
- *19 13 07\** aqueous liquid wastes and aqueous concentrates from groundwater remediation containing dangerous substances
- *19 13 08* aqueous liquid wastes and aqueous concentrates from groundwater remediation other than those mentioned in *19 13 07*

# 20 MUNICIPAL WASTES (HOUSEHOLD WASTE AND SIMILAR COMMERCIAL, INDUSTRIAL AND INSTITUTIONAL WASTES) INCLUDING SEPARATELY COLLECTED FRACTIONS

20 01 separa	ately collected fractions (except 15 01)
20 01 01 20 01 01	paper and cardboard
20 01 02	glass
20 01 08	biodegradable kitchen and canteen waste
20 01 10	clothes
20 01 11	textiles
20 01 13*	solvents
20 01 14*	acids
20 01 15*	alkalines
20 01 17*	photochemicals
20 01 19*	pesticides
20 01 21*	fluorescent tubes and other mercury-containing waste
20 01 23*	discarded equipment containing chlorofluorocarbons
20 01 25	edible oil and fat
20 01 26*	oil and fat other than those mentioned in 20 01 25
20 01 27*	paint, inks, adhesives and resins containing dangerous substances
20 01 28	paint, inks, adhesives and resins other than those mentioned in 20 01 27
20 01 29*	detergents containing dangerous substances
20 01 30	detergents other than those mentioned in 20 01 29
20 01 31*	cytotoxic and cytostatic medicines
20 01 32	medicines other than those mentioned in 20 01 31
20 01 33*	batteries and accumulators included in 16 06 01, 16 06 02 or 16 06 03
	and unsorted batteries and accumulators containing these batteries
20 01 34	batteries and accumulators other than those mentioned in 20 01 33
20 01 35*	discarded electrical and electronic equipment other than those
	mentioned in 20 01 21 and 20 01 23 containing hazardous components
20 01 36	discarded electrical and electronic equipment other than those
	mentioned in 20 01 21, 20 01 23 and 20 01 35
20 01 37*	wood containing dangerous substances
20 01 38	wood other than that mentioned in 20 01 37
20 01 39	plastics
20 01 40	metals
20 01 41	wastes from chimney sweeping
20 01 99	other fractions not otherwise specified

# 20 02 garden and park wastes (including cemetery waste)

- 20 02 01 biodegradable waste
- 20 02 02 soil and stones
- 20 02 03 other non-biodegradable wastes

#### 20 03 other municipal wastes

- 20 03 01 mixed municipal waste
- 20 03 02 waste from markets
- 20 03 03 street-cleaning residues
- 20 03 04 septic tank sludge
- 20 03 06 waste from sewage cleaning
- 20 03 07 bulky waste
- 20 03 99 municipal wastes not otherwise specified

#### **APPENDIX B**

#### **B-1: Mining Industry and Processes**

Naturally occurring substances are usually divided into metalliferous ores, such as the ores of gold, iron, copper, lead, zinc, tin, and manganese, and nonmetalliferous minerals, such as coal, quartz, bauxite, trona, borax, asbestos, talc, feldspar, and phosphate rock [22].

According to European Waste Catalogue these wastes related to extracted minerals are separated as metalliferous minerals and non-metalliferous minerals as well [19].

The initial step of the mining and mineral processing operations is the actual removal of the mineral value in ore from the host rock or matrix. Mining can be categorized as surface mining, underground mining, and in situ mining. Surface mining is used to excavate ores at or close to the earth's surface. The term surface mining includes open pit mining, highwall or strip mining, which is used to excavate coal or other deposits, and dredging to excavate placer deposits. Underground and in situ mining both remove minerals from deeper deposits. In underground mining minerals are extracted from subsurface layers. In situ mining utilizes injection and extraction wells for the purpose of leaching ore in place [29].

Following the extraction step, minerals or ores are subjected to various processes for the purpose of increasing the concentration of desired material in the ore. This step is known as beneficiation, which can be subcategorized as leaching and milling. In milling, the valuable portion is separated from less valuable rock called gangue by mainly using physical differences of desired portion and gangue or simply by crushing the ore and separating desired portion. Beneficiation methods include gravity concentration, which includes coarse/fine concentrations, amalgamation and sink/float separation, magnetic separation, electrostatic separation and flotation [29].

Leaching is the process of extracting a soluble metallic compound from an ore by selectively dissolving it in a suitable solvent, such as water, sulfuric acid, or sodium cyanide solution. The target metal is then removed from the "pregnant" leach solution by one of several electrochemical or chemical means [29]. The leaching process consists of preleaching activities, the actual leaching operation, and the recovery of the mineral value from the pregnant leach liquor [29]. Preleaching activities include roasting to alter the compound to drive off impurities and decrease water content and autoclaving, which convert the ore to an oxide form that is more amenable for leaching operations. Types of leaching operations are dump leaching, heap leaching and tank leaching according to the place which leaching operation is undertaken. Leachants include acids, cyanide and water. After the valuable materials must be separated from leachants by using methods such as precipitation, electrowinning, carbon adsorption, cementation, and solvent extraction [29].

There are a variety of mineral processing operations, including the following major categories: pyrometallurgical operations (e. g., smelting, refining, roasting), hydrometallurgical operations (e. g., digestion of phosphate in producing phosphoric acid), and electrometallurgical operations (e. g., electrolytic refining) [29]. Mineral processing may be further categorized as primary or secondary. Broadly defined, primary mineral processing is focused on processing concentrates from extraction and beneficiation of raw ores whereas secondary-processing focuses on recycling metals or minerals [29]. Wastes arising from these activities are covered under the entry of wastes from thermal processes.

#### **B-2: Wood Preservation Processes**

A wide variety of chemicals are used to preserve wood. The most commonly used chemicals are pentachlorophenol, creosote, and inorganic arsenical and/or chromate salts [33].

Pentachlorophenol is one of a group of synthetic organic compounds, called chlorophenols, which are commercially manufactured by reacting chlorine with phenol. Pentachlorophenol formulations are used primarily to treat poles, crossarms, lumber, timbers, and fence posts. Pentachlorophenol is used in a wide variety of solvents, including heavy petroleum (fuel oils) and creosote oils, light petroleum solvents such as butane, and volatile solvents such as liquefied petroleum gas (LPG), alcohols, and methylene chloride. Waxes and resins may also be added to pentachlorophenol formulations to prevent crystallization or "blooming" of the pentachlorophenol on the wood surface as the solvent evaporates [33].

Commercial pentachlorophenol used in wood preserving contains approximately 83 percent pentachlorophenol, 6 percent tetrachlorophenol, 6 percent other chlorinated phenols, and 5 percent impurities (chlorine compounds and inert materials). Pentachlorophenol and chlorophenate impurities have been found to include the tetra- to octa-chlorinated dioxins and furans [33].

Creosote generically refers to mixtures of relatively heavy residual oils obtained from the distillation of tar or crude petroleum. Creosote formulations are used primarily in treating railroad ties, fence posts, lumber and timbers, crossarms, poles, and marine and fresh-water piling. Although creosotes can be derived from a variety of tars, including wood-, petroleum-, and coalbased tar derivatives, creosote formulations also include creosote solutions, in which creosote is blended with petroleum oils or crude coal tar, and creosotes fortified with insecticide additives such as pentachlorophenol, arsenic trioxide, copper compounds, or malathion. The use of insecticide-fortified creosote has been limited [33].

Inorganic preservatives consist of arsenical and chromate salts and fluorides dissolved in water. Inorganic arsenical and/or chromate formulations are used primarily for the treatment of lumber and timber for the building industry. According to a RCRA 3007 Survey conducted in 1985, the most commonly used inorganic preservatives include:

- Chromated Copper Arsenate (CCA);
- Ammoniacal Copper Arsenate (ACA);
- Acid Copper Chromate (ACC);
- Chromated Zinc Chloride (CZC); and
- Fluor-Chrome-Arsenate-Phenol (FCAP) [33].

Three formulations of CCA (Types A, B, and C) are currently used at wood preserving plants [33].

#### **B-2.1** Conditioning Processes

Wood preserving consists of the application of preservative chemicals to wood to protect against decay and deterioration. Surface discoloration (sapstaining) can be adequately controlled by applying a superficial coat of preservative, but for long-lasting effectiveness, deep and uniform penetration of preservative into the wood is required. This type of penetration can only be achieved if the wood has been properly conditioned before the preservative is applied [33].

Seasoning and mechanical conditioning are the two most commonly used conditioning methods. Seasoning reduces the moisture content of freshly-cut wood to a point where the preservative can penetrate and be retained by the cells of the wood. Mechanical conditioning consists of physically preparing the wood to improve the penetrability of the preservative, usually by making holes or incisions along the wood surface. Untreated wood may undergo either one or both of these conditioning methods before to preservative application [33].

Seasoning conditioning methods include: (1) steaming wood at elevated pressure in a retort followed by application of a vacuum; (2) kiln drying; (3) heating wood in a preservative bath under reduced pressure in a retort (Boulton process); (4) heating unseasoned wood in a solvent (vapor drying); and (5) drying wood in yards, at ambient temperatures (air seasoning) [33].

In steam conditioning unseasoned or partially seasoned wood is subjected to direct steam impingement at an elevated pressure in a closed vessel. In kiln drying as the name implies lumber or poles are placed in dry kilns in which air is either crosscirculated or circulated from one end to the other. Drying temperatures and times vary with wood species and type of product. Boulton conditioning consists of heating wood in a preservative formulation in a pressure treating cylinder under vacuum conditions. The preservative, which has a boiling point higher than the boiling point of water, serves as a heat transfer medium. After the temperature in the treating cylinder is raised to operating temperature, a vacuum is drawn and water vaporizes from the wood, passes through the preservative bath, and collects in a condenser. Vapor conditioning (vapor drying) consists of exposing wood in a closed vessel to vapors from one of many organic chemicals that are immiscible with water and have initial boiling points ranging from 100°C to 204°C. Air drying consists of simply allowing wood to dry at ambient temperatures in storage yards [33].

According to the RCRA 3007 Survey, the majority of plants treating with creosote and pentachlorophenol condition wood by air drying, kiln drying, or steaming. Plants treating with inorganics, however, almost exclusively use kiln drying [33].

#### **B-2.2** Preservative Application Processes

After conditioning, preservatives may be applied by either pressure or nonpressure processes. Pressure processes for applying wood preservatives employ a combination of air and hydrostatic pressure and vacuum. There are two basic types of pressure treatment processes, distinguished by the particular sequence of application of vacuum and pressure. The first pressure method is referred to in the industry as the "empty cell" process. The second pressure method, known as the "full cell" process, results in higher retention of preservative but in limited penetration compared to the empty cell process. There is no difference in the types of wastes generated by full cell and empty call processes, although wood treated by the full cell process may drip more and has a greater tendency to bleed than wood treated by the empty cell process [33].

A vacuum-only preservative process is also used in the wood preserving industry. The vacuum-only process is performed by enclosing wood in an airtight container, pulling an initial vacuum, and adding preservative solution to atmospheric pressure [33].

Nonpressure processes including brushing or spraying, dipping, soaking (steeping), and thermal applications. In the brushing and spraying methods of preserving wood, the preservative is applied to the surface of the wood in a thick layer and is allowed to soak in. Dipping is essentially the same as spraying or brushing in terms of the types of preservatives used and conditioning requirements except that it generally uses more preservative and requires more equipment, namely, a dip tank of sufficient size. Soaking at ambient temperature involves immersing wood in an unheated oil solution (commonly a pentachlorophenol formulation) for periods ranging from 2 days to 1 week. The thermal process, or hot and cold bath process, involves immersing seasoned wood in successive baths of hot and cool preservatives. The hot baths expand the outer layers of the timbers and evaporate moisture through the surface of the wood. The cold bath causes the air and vapor in the outer shell of the wood to contract, thereby forming a partial vacuum [33].

#### **B-3: Petroleum Refining Processes**

The primary products of the industry fall into three major categories: fuels (motor gasoline, diesel and distillate fuel oil, liquefied petroleum gas, jet fuel, residual fuel oil, kerosene, and coke); finished nonfuel products (solvents, lubricating oils, greases, petroleum wax, petroleum jelly, asphalt, and coke); and chemical industry feedstocks (naphtha, ethane, propane, butane, ethylene, propylene, butylenes, butadiene, benzene, toluene, and xylene). The variety of end-products in petroleum refining is given in Figure B-3.1[37].

Crude oil is a mixture of many different hydrocarbons and small amounts of impurities. The composition of crude oil can vary significantly depending on its source. Petroleum refineries are a complex system of multiple operations and the operations used at a given refinery depend upon the properties of the crude oil to be refined and the desired products. For these reasons, no two refineries are alike [37].

However, a summary of processes used in petroleum refineries is given below in order to give a general understanding about the overall petroleum refining process.

Refining crude oil into usable petroleum products can be separated into two phases and a number of supporting operations. The first phase is desalting of crude oil and the subsequent distillation into its various components or "fractions" [37]. Crude oil contains many impurities in the form of inorganic compounds such as salts, sand and silt. These impurities especially salts have detrimental effects on catalytic reactions and on heat exchangers since they lead to corrosion [38]. Since these salts are watersoluble it is important to remove water from the crude oil before processing of oil begins. For this reason either a demulsifying chemical is added or a high potential electric field is applied [37].



**Figure B-3. 1 Petroleum refining products** 

A further distillation of the lighter components and naphtha is carried out to recover methane and ethane for use as refinery fuel, LPG (liquefied petroleum gaspropane and butane), gasoline blending components and petrochemical feedstocks. First of these distillation processes is atmospheric distillation in which crude oil is heated to elevated temperatures and subjected to distillation under atmospheric pressure [38]. Fractions with lower boiling point are condensed at the top of the distillation column and heavier fractions cannot volatilize and remain at the bottom of the column [35]. Lighter fractions include naphtha and light components such as ethane and methane, kerosene and light gas oil. Heavy fractions include heavy gas oil and atmospheric residues [38].

The main objective of the vacuum distillation is to process the bottom products of atmospheric distillation process by applying vacuum thus decreasing the pressure and increasing volatilization of heavier fractions. Products from vacuum distillation are light vacuum gas oil, heavy vacuum gas oil and vacuum residue. Vacuum distillation produces feedstock for cracking unit, coking, bitumen and base oil units [35].

The second phase is made up of different types of downstream processes: combining breaking and reshaping the fractions. These processes change the molecular structure of hydrocarbon molecules either by breaking them into smaller molecules, joining them to form larger molecules or reshaping them into higher quality molecules. [37]. Downstream processes include thermal cracking (visbreaking), coking, catalytic cracking, catalytic hydrocracking, hydrotreating, alkylation, isomerization, polymerization, catalytic reforming, solvent extraction, merox, dewaxing, propane deasphalting and other operations.

In thermal cracking or visbreaking, heat and pressure is used to break large hydrocarbon molecules into smaller, lighter molecules. Thermal cracking is replaced by catalytic cracking in most of the refineries nowadays [37]. The main difference of catalytic cracking from thermal cracking is the additional use of a catalyst besides heat and pressure in order to break the large hydrocarbon molecules.

Coking is a cracking process used primarily to reduce refinery production of low-value residual fuel oils to transportation fuels, such as gasoline and diesel [37]. The products from the coking fractionator are refinery fuel gas, LPG, naphtha and light and heavy gas oils. Petroleum coke is another product with the type depending upon the process used, operating conditions and feedstock used [38].

In catalytic hydrocracking cracking occurs under pressure and in the presence of hydrogen. The hydrogen suppresses the formation of heavy residual material and increases the yield of gasoline by reacting with the cracked products. [37].

Alkylation is used to produce a high octane gasoline blending stock from the isobutane formed primarily during catalytic cracking and coking operations, but also from catalytic reforming, crude distillation and natural gas processing. Alkylation joins an olefin and an isoparaffin compound using either a sulfuric acid or hydrofluoric acid catalyst. The products are alkylates including propane and butane liquids [37].

Supporting operations are those not directly involved in the production of hydrocarbon fuels but serving in a supporting role. They may include energy generation, wastewater treatment, sulfur recovery, additive production, waste gas treatment, blowdown systems, handling and blending of products and storage of products.

#### **B-4: Inorganic Chemical Processes**

B-4.1 Processes for Manufacture of Acids

#### B-4.1.1 Sulfuric Acid Production

Sulphuric acid ( $H_2SO_4$ ) is a basic raw material used in a wide range of industrial processes and manufacturing operations. Almost 70% of sulfuric acid is used in the production of phosphate fertilizers [97]. Other important applications of sulfuric acid are found in petroleum refining, pigment production, steel pickling, non-ferrous metals extraction and the manufacture of explosive, detergents (organic sulfonation processes), plastics and man-made fibers [57].

The combustion of elemental sulfur is the predominant source of  $SO_2$  used to manufacture  $H_2SO_4$ . The combustion of hydrogen sulfide from waste gases, the thermal decomposition of spent sulfuric acid or other sulfur containing materials, and the roasting of pyrites are also used as sources of  $SO_2$  [97]. Sulphuric acid may be manufactu97red either by the lead chamber process or the contact process. However, contact process is widely used recently [97].

Contact plants are classified according to the raw materials charged to them; elemental sulfur burning, spent sulfuric acid and hydrogen sulfide burning, and metal sulfide ores and smelter gas burning [97].

The contact process incorporates three basic operations, each of which corresponds to a distinct chemical reaction. First, the sulfur in the feedstock is oxidized (burned) to sulfur dioxide. The resulting sulfur dioxide is fed to a process unit called a converter where it is catalytically oxidized to sulfur trioxide. Finally, the sulfur trioxide is absorbed in a strong sulfuric acid (98%) solution [97].

#### **Elemental Sulfur Burning Plants**



Flow diagram of a sulfuric acid plan burning elemental sulfur is given in Figure B-4.1.

Figure B-4. 1 Flow diagram of contact process sulfuric acid plant burning elemental sulfur [97]

In the Frasch process, elemental sulfur is melted, filtered to remove ash, and sprayed under pressure into a combustion chamber. The gases from the combustion chamber cool and then enter the catalyst (vanadium pentoxide) converter. After being cooled, again by generating steam, the converter exit gas enters an absorption tower. The absorption tower is a packed column where acid is sprayed in the top and the sulfur trioxide enters from the bottom. The sulfur trioxide combines with the water in the acid and forms more sulfuric acid [97].

In the dual absorption process, the  $SO_3$  gas formed in the primary converter stages is sent to an interpass absorber where most of the  $SO_3$  is removed to form  $H_2SO_4$ . The single absorption process uses only one absorber as the name implies [97].

Spent Acids or Hydrogen Sulfide Burning Plants

Flow diagram of a sulfuric acid plan that burns spent acid is given in Figure B-4.2. Two types of plants are used to process this type of sulfuric acid. In one, the sulfur dioxide and other combustion products from the combustion of spent acid and/or hydrogen sulfide with undried atmospheric air are passed through gas cleaning and mist removal equipment. The gas stream next passes through a drying tower. A blower draws the gas from the drying tower and discharges the sulfur dioxide gas to the sulfur trioxide converter, then to the oleum tower and/or absorber.

In a "wet gas plant," the wet gases from the combustion chamber are charged directly to the converter with no intermediate treatment. The gas from the converter flows to the absorber, through which 93 to 98% sulfuric acid circulates [98].

Sulfide Ores and Smelter Gas Plants

The configuration of this type of plant is essentially the same as that of a spent acid plant with the primary exception that a roaster is used in place of the combustion furnace.

The feed used in these plants is smelter gas, available from such equipment as copper converters, reverberatory furnaces, roasters and flash smelters. To remove the impurities, the gases must be cooled and passed through purification equipment consisting of cyclone dust collectors, electrostatic dust and mist precipitators, and scrubbing and gas cooling towers. After the gases are cleaned and the excess water vapor is removed, they are scrubbed with 98% acid in a drying tower. Beginning with the drying tower stage, these plants are nearly identical to the elemental sulfur plants



Figure B-4. 2Flow diagram of contact process sulfuric acid plant burning spent acid [97]

B-4.1.2 Hydrochloric Acid Production

Hydrochloric acid (HCl) is a versatile chemical that has a number of different industrial uses. Hydrochloric acid is also a common ingredient in many reactions and is the preferred acid for catalyzing organic processes [58].

Hydrochloric acid can be produced by one of the five following processes [58]:

1. Synthesis from elements:

$$H_2 + Cl_2 \rightarrow 2HCl$$
 Eqn (1)

2. Reaction of metallic chlorides, particularly sodium chloride (NaCl), with sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) r a hydrogen sulfate:

$$NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl$$
 Eqn (2)

$$NaCl + NaHSO_4 \rightarrow Na_2SO_4 + HCl$$
 Eqn (3)

$$2NaCl + H_2SO_4 \rightarrow Na_2SO_4 + 2HCl \qquad \text{Eqn (4)}$$

3. As a byproduct of chlorination, e.g. in the production of dichloromethane, trichloroethylene, perchloroethylene, or vinyl chloride:

$$C_2H_4 + Cl_2 \rightarrow C_2H_4Cl_2 \qquad \qquad \text{Eqn} (5)$$

$$C_2H_4Cl_2 \rightarrow C_2H_3Cl + HCl$$
 Eqn (6)

4. By thermal decomposition of the hydrated heavy-metal chlorides from spent pickle liquor in metal treatment:

$$2FeCl_3 + 6H_2O \rightarrow Fe_2O_3 + 3H_2O + 6HCl \qquad \text{Eqn} (7)$$

5. From incineration of chlorinated organic waste:

$$C_4H_6Cl_2 + 5O_2 \rightarrow 4CO_2 + 2H_2O + 2HCl$$
 Eqn (8)

#### B-4.1.3 Hydrofluoric Acid Production

Hydrogen fluoride is produced in two forms, as anhydrous hydrogen fluoride and as aqueous hydrofluoric acid. The predominant form manufactured is anhydrous hydrogen fluoride, a colorless liquid or gas which fumes on contact with air and is water soluble [98].

Traditionally, hydrofluoric acid (HF) has been used to etch and polish glass. Currently, the largest use for HF is in aluminum production. Other HF uses include uranium processing, petroleum alkylation, and stainless steel pickling. Hydrofluoric acid is also used to produce fluorocarbons used in aerosol sprays and in refrigerants [98].

Hydrofluoric acid is manufactured by the reaction of acid-grade fluorspar  $(CaF_2)$  with sulfuric acid  $(H_2SO_4)$  [97].

Flow diagram of hydrofluoric acid production is given in Figure B-4.3.


Figure B-4. 3Hydrofluoric acid process flow diagram [98]

Dry fluorspar and a slight excess of sulfuric acid are fed continuously to the front end of a stationary prereactor or directly to the kiln. The prereactor mixes the components prior to charging to the rotary kiln. Calcium sulfate (CaSO<sub>4</sub>) is removed at the opposite end of the kiln. The gaseous reaction products—hydrogen fluoride and excess H<sub>2</sub>SO<sub>4</sub> from the primary reaction, silicon tetrafluoride (SiF<sub>4</sub>), sulfur dioxide (SO<sub>2</sub>), carbon dioxide (CO<sub>2</sub>), and water produced in secondary reactions—are removed from the front end of the kiln along with entrained particulate. The particulates are removed from the gas stream by a dust separator and returned to the kiln. Sulphuric acid and water are removed by a precondenser. Hydrogen fluoride vapors are then condensed in refrigerant condensers forming "crude HF," which is removed to intermediate storage tanks. The remaining gas stream passes through a sulfuric acid absorption tower or acid scrubber, removing most of the remaining hydrogen fluoride and some residual sulfuric acid, which are also placed in intermediate storage. The gases exiting the scrubber then pass through water scrubbers, where the SiF<sub>4</sub> and remaining HF are recovered as fluosilisic acid (H<sub>2</sub>SiF<sub>6</sub>). The hydrogen fluoride and sulfuric acid are delivered from intermediate storage tanks to distillation columns, where the hydrofluoric acid is extracted at 99.98% purity. Weaker concentrations (typically 70 to 80%) are prepared by dilution with water [98].

# B-4.1.4 Phosphoric Acid Production

Phosphoric acid is the most important mineral acid in terms of volume and value after sulfuric acid. Phosphoric acid is primarily used in the manufacture of phosphate salts and its direct use as an acid is secondary [57]. Phosphoric acid can be manufactured using a thermal or wet process.

### Thermal Process

Raw materials for the production of phosphoric acid by the thermal process are elemental (yellow) phosphorus, air, and water. Thermal process phosphoric acid manufacture involves three major steps listed below:

- <u>Combustion</u>: Elemental phosphorus is produced from phosphate rock, coke and silica in an electrical resistance furnace. The liquid elemental phosphorus is burned (oxidized) in ambient air in a combustion chamber to form phosphorus pentoxide.
- <u>Hydration</u>: The phosphorus pentoxide is then hydrated with dilute phosphoric acid (H<sub>3</sub>PO<sub>4</sub>) or water to produce strong phosphoric acid liquid
- <u>Demisting</u>: Demisting, the final step, removes the phosphoric acid mist from the combustion gas stream before release to the atmosphere. This is usually done with high-pressure-drop demisters [98].

Thermal acid s considerably purer than acid produced by the wet-process, but it is also more expensive and is hence produced in much smaller quantities [57].

## Wet Process

The second types of processes are those using phosphate minerals, which are decomposed with an acid. There are three possible subgroups of wet processes depending on which acid is used for the acidulation i.e. nitric, hydrochloric or sulfuric acid. The wet digestion of phosphate rock with sulfuric aid is the preferred process in terms of volume [57].

In this process, the phosphate rock is dried, crushed, and then continuously fed into the reactor along with sulfuric acid. The reaction combines calcium from the phosphate rock with sulfate, forming calcium sulfate (CaSO<sub>4</sub>), commonly referred to as gypsum. Gypsum is separated from the reaction solution by filtration [98]. Production process can be either of 5 processes listed below:

- Dihydrate process
- Hemihydrate process
- Hemihydrate recrystallisation process
- o Hemihydrate/dihydrate process
- Dihydrate/hemihydrate process [57]
- B-4.1.5 Nitric Acid Production

Nitric acid is a strong acid that occurs only in nature in the form of its nitrate salts. A weak acid or strong acid can be produced depending on the application required [57].

Nitric acid is produced by two methods. The first method utilizes oxidation, condensation, and absorption to produce a weak nitric acid. Weak nitric acid can have concentrations ranging from 30 to 70% nitric acid. The second method combines dehydrating, bleaching, condensing, and absorption to produce high strength nitric acid from weak nitric acid. High strength nitric acid generally contains more than 90% nitric acid [80].

# Weak Nitric Acid Production

Weak nitric acid production consists of three steps [80]:

- <u>Ammonia oxidation</u>: Ammonia/air mixture is oxidized as a result of which nitric oxide is obtained.
- <u>Nitric oxide oxidation</u>: The nitric oxide reacts noncatalytically with residual oxygen to form nitrogen dioxide and its liquid dimer, nitrogen tetroxide
- <u>Absorption</u>: The final step introduces the nitrogen dioxide/dimer mixture into an absorption process after being cooled. An aqueous solution of 55 to 65%

(typically) nitric acid is withdrawn from the bottom of the tower. The acid concentration can vary from 30 to 70% nitric acid.

There are two basic types of systems used to produce weak nitric acid: single-stage pressure process, and dual-stage pressure process [80]. In the past, nitric acid plants have been operated at a single pressure; newer plants tend to operate a dual-stage pressure system, incorporating a compressor between the ammonia oxidizer and the condenser.

### Strong Nitric Acid Production

High strength nitric acid (98 to 99% concentration) can be obtained by concentrating weak nitric acid (30 to 70% concentration) using extractive distillation. The distillation must be carried out in the presence of a dehydrating agent. Concentrated sulfuric acid (typically 60% sulfuric acid) is most commonly used for this purpose [80].

The strong sulfuric acid and weak nitric acid is introduced to a dehydrating column. The concentrated acid vapor leaves the column and goes to a bleacher and a countercurrent condenser system to effect the condensation of strong nitric acid and the separation of oxygen and nitrogen oxide by-products.

#### B-4.1.6 Boric Acid Production

The chemical formula for boric acid, also known as boracic acid, borofax, hydrogen orthoborate, and orthoboric acid, is  $H_3BO_3$ . It is generally a colorless, crystalline powder. Uses for boric acid are extremely varied.

There are currently no reported facilities in European Union producing boric acid however; two facilities in United States produce boric acid namely IMC Chemicals Inc. and U.S. Borax Inc. in California [59]. IMC Chemicals Inc.

IMCC's boric acid production can be broken up into two sequential processes: the liquid-liquid extraction (LLX) process and the crystallization and evaporation process. Flow diagram is given in Figure B-4.4 **Error! Reference source not found.**and Figure B-4.5.



Figure B-4. 4Flow diagram of IMC Chemicals Inc. [59]



# **Figure B-4. 5 Flow diagram of IMC Chemicals Inc. (continued) [59]** Steps of liquid-liquid extraction (LLX) process are given below:

- Highly mineralized brine is mixed with an organic extractant (chelating agent) in a kerosene solution. This step generates partially depleted brine (Bevill exempt).
- The loaded extractant then is sent through strippers where it is mixed with dilute sulfuric acid to strip the boron, potassium, and sodium from the extractant forming a boric acid, sodium sulfate, and potassium sulfate solution (referred to as strip solution). This step produces a stripped extractant, referred to as barren extractant.
- The strip solution enters the final strip solution (FSS) settler where the separation of mineral rich liquor and aqueous/organic emulsion (crud) occurs. At this point in the process, the FSS liquor is sent to the crystallization and evaporation process. [59]

Steps of crystallization and evaporation processes are given below:

- The FSS liquor passes through two tanks. Carryover crud separates from the liquor in the tanks and is sent to the crud treatment facility.
- The FSS liquor is fed to a carbon column to remove any remaining organic substances. On a weekly basis, the carbon from the carbon column is cleaned in the carbon cleaning system (washing and regeneration in a furnace). This generates wash waters and regenerated carbon.
- From the carbon column, the FSS liquor is sent to the second effect crystallizer evaporator producing a slurry of boric acid crystals suspended in liquor. The slurry settles, with the solids going to a centrifuge and the liquid going through the first effect crystallizer evaporator.
- In the centrifuge, additional liquid is removed and is sent to the first effect crystallizer evaporator to separate out the sodium sulfate and potassium sulfate.
- Boric acid crystals, are washed with water and sent through a rotary dryer. After drying, the crystals are cooled, screened and stored prior to packaging for customers. Air generated from the rotary dryer is sent through a scrubber. The scrubber water is sent to the Trona skimmer. [59]

U.S Borax Inc.

U.S. Borax mines sodium borate kernite ore to produce boric acid through a process of dissolution, classification, thickening, filtration and crystallization. Flow diagram is given in Figure B-4.6.



Figure B-4. 6 Flow diagram of U.S. Borax Inc. [59]

Steps of the production process are given below:

- <u>Extraction, Crushing and Sizing</u>: Kernite ore consisting of various boron compounds (borate values), clays, sands, and other insolubles is extracted from the on-site mine, crushed and sized.
- Dissolution: The ore is transported to a dissolving/leaching unit where the ore is mixed with mother liquor. The mother liquor dissolves or leaches the borate from clays, sand and other insolubles that make up the ore. The resulting ore slurry is conveyed to classifiers for removal of coarse insolubles. The dissolution/leaching step generates ore dust and vapor waste streams that are captured in a scrubber. A liquid waste stream is bled from the scrubber and sent to the tailings tank.

- <u>Classification (Gravity Separation)</u>: The slurry is sent through a series of rake classifiers, which physically separate the clay, sand and other coarse insolubles (gangue) from the slurry. The remaining crude strong liquor drains from the gangue in the classifiers and is sent to a settler. This step generates gangue solids and liquids and fine ore insolubles (tailings).
- <u>Thickening (Gravity Concentration)</u>: The crude strong liquor from the classifiers is then transferred to settlers and washers to further separate out ore solids. The underflow is diluted with mother liquor and further settled. The underflow from the washer is discharged to the tailings tank. This step generates a continuous underflow consisting of fine ore solids and liquid (tailings) from the settlers and washers.
- <u>Filtration</u>: The crude strong liquor is filtered to remove any trace of insoluble ore material. This step generates filter wastes, consisting of filter aid, spent filters, and filter rinse wastewater.
- <u>Crystallization:</u> The filtered crude strong liquor is fed to the crystallizer to form boric acid crystals. A bleed stream continuously discharges from the cooling tower to remove carryover impurities. The crystals are separated from the residual liquor through filtration and are washed. Most of the filtrate is reused as mother liquor. A small bleed stream is also generated during the filtration and washing step. The crystals are then dried and packaged for customers [59].

#### B-4.1.7 Chromic Acid Production

Chromic acid (CrO<sub>3</sub>), also known as chromium trioxide or chromic anhydride, can be produced by more than one method. The traditional chromic acid production process involves mixing sodium dichromate dihydrate with sulfuric acid in a reactor, which is heated externally and stirred with a sweep agitator. The agitator is turned off, and the mixture separates into a heavy layer of molten chromic acid and a light layer of sodium bisulfate. The chromic acid layer is tapped from the reactor and flaked on water-cooled rolls to produce the commercial product [99].

In the second production process, a large amount of sulfuric acid is first added to a concentrated solution of sodium dichromate. A crude chromic acid containing sodium bisulfate and some sulfuric acid is precipitated and separated by filtration. The crude chromic acid is then melted in this small amount of sodium bisulfate, with sodium dichromate added to convert any excess sulfuric acid into chromic acid. The chromic acid is then flaked as in the traditional process, packaged and sold. Less waste sodium bisulfate is produced by this process than by the traditional chromic acid manufacturing process [99]. Flow diagram of this process is given Figure B-4.7.



Figure B-4.7 Chromic acid production [99]

# B-4.2 Explosive Manufacture Processes

Propellants and explosives are materials, which, under the influence of thermal or mechanical shock, decompose rapidly and spontaneously with the evoluation of a great deal of heat and much gas. Some of the most common industrial and military propellants and explosives include gunpowder, nitrocellulose, nitroglycerin, ammonium nitrate, trinitrotoluene (TNT), picric acid, ammonium picrate, RDX, HMX, and lead azide. [61].

# B-4.2.1 Production of Dinitrotoluene and Trinitrotoluene

The first stage of nitration of toluene using nitric acid, in the presence of sulfuric acid, resulting in dinitrotoluene. [99] Nitration of toluene is given in Figure B-4.8.



Figure B-4. 8Nitration of toluene to form nitrotoluene [101]

The production of TNT follows the same chemical process, regardless of whether batch or continuous method is used. The flow chart for TNT production is shown in Figure B-4.9.



Figure B-4. 9TNT production [101]

The production of TNT by nitration of toluene is a 3-stage process performed in a series of reactors. The mixed acid stream is shown to flow countercurrent to the flow of the organic stream. Toluene and spent acid fortified with a 60 percent  $HNO_3$  solution are fed into the first reactor. The organic layer formed in the first reactor is pumped into the second reactor, where it is subjected to further nitration with acid from the third reactor fortified with additional HNO<sub>3</sub>. The product from the second nitration step, a mixture of all possible isomers of dinitrotoluene (DNT), is pumped to the third reactor. In the final reaction, the DNT is treated with a fresh feed of nitric acid and oleum (a solution of sulfur trioxide  $[SO_3]$  in anhydrous sulfuric acid). The crude TNT from this third nitration consists primarily of 2,4,6-trinitrotoluene. The crude TNT is washed to remove free acid, and the wash water (yellow water) is recycled to the early nitration stages. The washed TNT is then neutralized with soda ash and treated with a 16 percent aqueous sodium sulfite (Sellite) solution to remove contaminating isomers. The Sellite waste solution (red water) from the purification process is discharged directly as a liquid waste stream, is collected and sold, or is concentrated to a slurry and incinerated. Finally, the TNT crystals are melted and passed through hot air dryers, where most of the water is evaporated. The dehydrated product is solidified, and the TNT flakes packaged for transfer to a storage or loading area [101].

# B-4.2.2 Production of Nitrocellulose

Nitrocellulose is commonly prepared by the batch-type mechanical dipper process. A newly developed continuous nitration processing method is also being used. In batch production, cellulose in the form of cotton linters, fibers, or specially prepared wood pulp is purified by boiling and bleaching. The dry and purified cotton linters or wood pulp are added to mixed nitric and sulfuric acid in metal reaction vessels known as dipping pots. The reaction is represented by:

 $(C_{6}H_{7}O_{2}(OH)_{3})_{x} + 3HONO_{2} + H_{2}SO_{4} \rightarrow (C_{6}H_{7}O_{2}(ONO_{2})_{3})_{x} + 3H_{2}O + H_{2}SO_{4} \quad Eqn (9)$ Cellulose Nitric Sulfuric Nitrocellulose Water Sulfuric acid acid acid

Following nitration, the crude nitrocellulose is centrifuged to remove most of the spent nitrating acids and is put through a series of water washing and boiling treatments to purify the final product. [101]. Production process of Kırıkkale Nitroselüloz Ticaret ve Sanayii A.Ş. is given in Figure B-4.10.

# B-4.2.3. Production of Nitroglycerine

Nitroglycerine is produced by mixing glycerine with concentrated nitric and sulfuric acids, similar to the TNT manufacturing process. The acids are then decanted, and the nitroglycerine is washed with water and soda ash to remove any residual acids.



Figure B-4. 10 Nitrocellulose production

# B-4.2.4 Production of Smokeless Powder

Smokeless powders they may be considered to be of two classes: (1) singlebase powders, and (2) multi- (double or triple) base powders.

In the single-base powders, cellulose nitrates (nitrocellulose) form the only explosive ingredient. The other materials present in single-base powders are included to obtain suitable form, desired burning characteristics, and stability. Production process of Kırıkkale Nitroselüloz Ticaret ve Sanayii A.Ş. is given in Figure B-4.11.

In the double- or triple-base powders, nitroglycerin is present to assist in dissolving the nitrocellulose during manufacture, as well as to add to the explosive qualities [102]. Production process of Kırıkkale Nitroselüloz Ticaret ve Sanayii A.Ş. is given in Figure B-4.12.



Figure B-4. 11Single base powder production



Figure B-4. 12 Double base powder production

#### B-4.3 Processes for Manufacture of Bases

#### B-4.3.1 Calcium Hydroxide Production

Quicklime, or burnt lime, is calcium oxide (CaO) produced by decarbonisation of limestone (CaCO<sub>3</sub>). Slaked lime are produced by reacting, or "slaking", quicklime with water and consist mainly of calcium hydroxide (Ca(OH)<sub>2</sub>). Slaked lime includes hydrated lime (dry calcium hydroxide powder), milk of lime and lime putty (dispersions of calcium hydroxide particles in water). The term lime includes quicklime and slaked lime and is synonymous with the term lime products [62].

The lime making process consists of the burning of calcium and/or magnesium carbonates at a temperature between 900 and 1500 °C, which is sufficiently high to liberate carbon dioxide, and to obtain the derived oxide (CaCO<sub>3</sub>  $\rightarrow$  CaO + CO<sub>2</sub>). For some processes significantly higher burning temperatures are necessary, for example dead-burned dolomite [62].

The calcium oxide product from the kiln is generally crushed, milled and/or screened before being conveyed to silo storage. From the silo, the burned lime is either delivered to the end user for use in the form of quicklime, or transferred to a hydrating plant where it is reacted with water to produce hydrated or slaked lime [62].

Lime processes mainly contain the following basic steps, which are illustrated in Figure B-4.13 [62]. These processes include:

- Winning of limestone: A typical mining process includes:
  - Removal of the overburden (i.e., the soil, clay and loose rock overlying the deposit).
  - o Blasting of rock.
  - Loading and transportation of the blasted rock to the crushing and screening plant.
- Limestone storage and preparation: Limestone is crushed to the appropriate size range, which is normally 5 to 200 mm depending upon the kiln used. Washing is sometimes used to remove natural impurities such as silica, clay and the very fine particles of limestone.
- Fuels storage and preparation: In lime burning, the fuel provides the necessary energy to calcine the lime. The fuel should be prepared as required for the

injection system, which can be of direct or indirect firing type. In the case of solid fuels, this involves delivery at the appropriate particle size for the installed handling system. In the case of liquid and gaseous fuels, the required pressure and (as appropriate) temperature need to be maintained.

- Calcination of limestone: The lime burning process typically involves:
  - Providing sufficient heat at above 800 °C to heat the limestone and to cause decarbonation, and
  - $\circ$  Holding the quicklime for the requisite time at a sufficiently high temperature (typically in the range 1200 to 1300 °C to adjust reactivity.

Shaft kilns, traveling grade kilns, top-shaped kilns, rotating heart kilns or rotary kilns can be used for calcinations of limestone.

- Quicklime processing: The objective of processing run-of-kiln (ROK) quicklime is to produce a number of grades with the particle sizes and qualities required by the various market segments. A number of unit processes are used, including screening, crushing, pulverizing, grinding, air-classifying and conveying.
- Quicklime hydration and slaking: Slaked lime includes hydrated lime (dry calcium hydroxide powder), milk of lime and lime putty (dispersions of calcium hydroxide particles in water).
- Storage, handling and transport [62]



Figure B-4. 13 Calcium hydroxide production [62]

### B-4.3.3 Ammonium Hydroxide Production

No data available exists regarding ammonium hydroxide production in Turkey therefore; ammonium hydroxide production processes is not covered.

B-4.3.3 Sodium Hydroxide Production

In Turkey sodium hydroxide production is accomplished only by chlor-alkali plants therefore, only this process will be covered. Chlor-alkali production processes are given in Section B-4.4. In this section information about sodium hydroxide in chlor-alkali plants is be presented.

Sodium hydroxide (caustic soda) is produced in a fixed ratio of 1.128 ton (as 100% NaOH) per ton chlorine produced [64].

The caustic soda solution from the three technologies is treated in slightly different ways due to the difference in composition and concentration [64].

In the mercury cell process, 50% caustic soda is obtained directly from the decomposers. The caustic soda is normally pumped through a cooler, then through a mercury removal system and then to the intermediate and final storage sections. In some cases the caustic is heated before filtration. The most common method for removal of mercury from caustic soda is a plate (or leaf) filter with carbon precoat. Under normal operating conditions, mercury-cell caustic soda (as 100% NaOH) contains 20-100 ppm of sodium chloride and 40-60  $\mu$ g Hg/kg NaOH<sup>2</sup>.

In the case of diaphragm and membrane technologies the caustic soda is concentrated by evaporation before final storage [64].

The caustic soda from membrane cells is of high quality, although the caustic soda produced (usually around 33% NaOH) needs concentration to 50% NaOH for some applications. The salt content of the membrane-cell caustic soda lies between 20-100 ppm (in 100% NaOH), but is on average slightly higher than mercury cell caustic [64].

In some plants the caustic soda is further concentrated to a 73% solution and to 100% as solid caustic prills or flakes. Some chlor-alkali production facilities can combine the caustic production process from mercury and membrane cells in order to minimize energy costs. It is possible to feed 33% caustic from the membrane cells to the decomposer to produce 50% caustic without the need for evaporation [64].

#### **B-4.4 Halogen Production Processes**

Halogen production covers production of chlorine, fluorine, bromine and iodine. However, no large scale production of fluorine, bromine and iodine currently occurs in Turkey, therefore, only production of chlorine will be covered in this study.

The chlor-alkali electrolysis process results in the manufacture of chlorine, hydrogen and sodium hydroxide (caustic) solution. The three basic processes for the electrolytic production of chlorine are 1) the diaphragm cell process, 2) the mercury cell process, and 3) the membrane cell process. In each process, a salt solution is electrolyzed by the action of direct electric current which converts chloride ions to elemental chlorine. The overall process reaction is:

$$2NaCl + 2H_2O \Rightarrow Cl_2 + H_2 + 2NaOH$$
 Eqn10

Each process represents a different method of keeping the chlorine  $(Cl_2)$  produced at the positive electrode (anode) separate from the caustic soda (NaOH) and hydrogen  $(H_2)$  produced, directly or indirectly, at the negative electrode (cathode).

Currently, only chlor-alkali processes applied in Turkey is membrane process. In this process, the anode and cathode are separated by a water-impermeable ionconducting membrane. Brine solution flows through the anode compartment where chloride ions are oxidized to chlorine gas. The sodium ions migrate through the membrane to the cathode compartment which contains flowing caustic soda solution. The demineralized water added to the catholyte circuit is hydrolyzed, releasing hydrogen gas and hydroxide ions. The sodium and hydroxide ions combine to produce caustic soda which is typically brought to a concentration of 32-35% by recirculating the solution before it is discharged from the cell. The membrane prevents the migration of chloride ions from the anode compartment to the cathode compartment; therefore, the caustic soda solution produced does not contain salt as in the diaphragm cell process. Depleted brine is discharged from the anode compartment and resaturated with salt. If needed, to reach a concentration of 50% caustic soda, the caustic liquor produced has to be concentrated by evaporation (using steam) [64].

Auxiliary processes include [64]:

- Salt unloading and storage: Brine is generally produced by the dissolving of fresh salt in water or depleted brine from membrane processes. The basic raw material is usually solid salt: rock salt, solar salt, or vacuum-evaporated salt from purifying and evaporating solution-mined brine.
- Brine purification and resaturation: Consists of primary purification (precipitation and filtration) and secondary purification (ion exchange). After brine purification dechlorination step by using activated carbon or reducing agent follows.
- Chlorine processing: Involves cooling, drying, compression, liquefication, handling and storage. After these steps, impurities such as water, hydrogen, nitrogen trichloride, bromine is removed.
- Caustic processing which is presented in Section B-4.3.1.
- Hydrogen processing

#### **B-5: Organic Chemical Processes**

B-5.1 Processes for Manufacture of Plastics, Synthetic Rubber and Man-made Fibers

The initial separation steps are carried out in refineries where a few natural sources of carbon (crude oil, natural gas and coal) are used to produce a limited number of high volume raw materials for the chemical industry (e.g. naphtha). Refineries export these raw materials to petrochemical plants where they are transformed by a complex combination of physical and chemical operations into a variety of base materials. These base materials are subjected to further sequences of processing which introduce functional groups to produce an even greater number of intermediates and monomers. The intermediates are converted to a large variety of fine products and polymers with high levels of functionalisation and high commercial value [57].

# B-5.1.1 Ethylene Cracking

Ethylene is a very important building block for the organic chemical industry and has wide range of derivatives (polyethylene, polystyrene, glycol, PVC etc.) [57].

Cracking is the process by which saturated hydrocarbons are converted into more sought after unsaturated species. It can be done either catalytically or thermally [57].

Catalytic cracking is used in refineries to convert the heavy (higher boiling) fractions into saturated, branched paraffins, naphthenes and aromatics [57].

In steam cracking process, suitable hydrocarbons are heated to very high temperatures, in the presence of steam, to split or "crack" the molecules into the desired lower olefin products. A cracker can be broken into three separate sections; pyrolysis, primary fractionation/compression and product fractionation [57].

The hydrocarbon feedstock is preheated in heat exchangers and then vaporized with superheated steam before passing into tubes arranged in a cracking furnace. By controlling the residence time, temperature profile and partial pressure, the hydrocarbon feedstock is cracked into smaller molecules (mainly ethylene, propylene etc.) [57].

The primary fractionator is used to condense out and fractionate fuel oil streams produced from naphtha and gas oil fed crackers. The gases are de-superheated in quench tower by a circulating oil or water stream. Tarry bottoms are removed from the system as product, which mostly fuels non-steam cracking furnaces and boilers. The product fractionation towers are used to separate the desired products. After separation, the ethylene still contains undesirable acetylene and ethane. Acetylene is either removed by catalytic hydrogenation or by extractive distillation [57].

# B-5.1.2 Polyethylene Production

Polyethylene is the most widely produced polymer worldwide. Depending on the physico-chemical properties of the product, different types of polyethylene are distinguished. The different product types require different production processes where the main distinction is the density of the final product [68].

Low density polyethylene (LDPE) is the oldest type of polyethylene. It is produced in a high pressure process. The high pressure LDPE process is very generic and the basic design does not change from company to company. The major variation is in reactor type, tubular versus autoclave which results in changes characteristics of product [68].

The slurry suspension and the gas phase processes are the two main categories of processes to produce high density polyethylene (HDPE). The main differences between processes and products produced by these processes are related to:

- The cooling mode applied. Evaporation and condensation of solvent, external cooling of the loop, cooling of the gaseous recycle flow, the latter potentially combined with a condensable solvent.
- o Mono or dual reactor systems
- The blend ratio of polymers produced in primary and secondary reactor.
- The capability of removing polymer waxes.
- The catalyst systems applied; Ziegler-Natta, chromium or metallocene catalysts.
- The type of solvent applied: ranges from supercritical propane to C9 solvent [89].

# B-5.1.3 Aromatics Production

The term "aromatics" is used to describe benzene, toluene, mixed xylenes, ortho-xylene, para-xylene and meta-xylene (commonly called as BTX) [57].

Some different pathways are possible for aromatics production based on processes applied and feedstocks used. Table B-5. 1 summarizes possible operations applied in aromatic plants.

As an example; aromatics production line in PETKİM aromatics plant consists of naphtha catalytic reforming process which occurs in ethylene cracking process and hydrogenation and pyrolysis of gasoline followed by separation of aromatics [69]

Process	Aim of process
1. Refining processes	
Hydrogenation of pygas	Hydrogenation of diolefins and desulphurization
Benzole pressure refining	Hydrogenation of coke oven benzole
Cyclar (UOP)	Aromatics from LPGs
2. Dealkylation processes	
Houdry Ritol	
Houdry, dealkylation	Production of benzene from toluene
(HDA)	
THDA (UOP)	Benzene from toluene by thermal route
3. Isomerization processes	
Octafining	Increasing the proportion of p-xylene
MAHI (Mobil)	p-xylenes from mixed xylenes
4. Transalkylation	
Arco	Product of benzene and C <sub>8</sub> aromatics from toluene
Totary	
Mobil LTD.	
5. Extraction processes	
Udex process	Extraction of aromatics
Sulfolane processes	
Arosolvan process	
IFP processes	
Morphylex process	
Carom (UOP)	
Glitsch GT-BTX	Bx/toluene from cat reformer feedstocks
6. Extractive distillation	
Distapex process	Production of aromatics
Morphylane process	
7. Crystallization processes	
Amoco process	Production p-xylene
8. Adsorption	
Parex(UOP)	p-xylene from mixed xylenes

 Table B-5. 1 Summary of typical processes for the production of aromatics [57]

### B-5.1.4 Ethylene Glycol and Ethylene Oxide Production

Ethylene oxide is a key chemical intermediate to the manufacture of many important products. Ethylene oxide is formed by reacting gaseous ethylene and oxygen over a solid, silver containing catalyst. Following reaction occurs:

$$C_2H_4 + \frac{1}{2}O_2 \xrightarrow{Ag} C_2H_4O$$
 Eqn (11)

Ethylene glycols are produced by reacting ethylene oxide with water. Mono ethylene glycol is formed by hydrolysis of ethylene oxide with water at elevated temperature and pressure according to following reaction [57].

$$C_2H_4O + H_2O \rightarrow HO - C_2H_4 - OH$$
 Eqn (12)

The main co-product in the mono ethylene glycol manufacturing process is diethylene glycol, which is formed by the reaction of mono ethylene glycol with ethylene oxide according to following reaction [68].

$$HO - C_2H_4 - OH + C_2H_4O \rightarrow HO - C_2H_4 - O - C_2H_4 - OH$$
 Eqn (13)

The diethylene glycol can further react again with ethylene oxide to form triethylene glycol and heavier glycols [57].

$$HO-C_{2}H_{4}-O-C_{2}H_{4}-OH+C_{2}H_{4}O \rightarrow HO-C_{2}H_{4}-O-C_{2}H_{4}-O-C_{2}H_{4}-OH \quad \text{Eqn (14)}$$

# B-5.1.5 Acrylonitrile Production

Acrylonitrile is an intermediate monomer used world-wide for several applications such as production of acrylic fiber and ABS. The BP/SOHIO process is the most commonly applied process for the production of acrylonitrile. The process is a vapor phase, exothermic ammoxidation of propylene using excess ammonia in the presence of an air-fluidized catalyst bed. The catalyst is a mixture of heavy metal oxides (mainly molybdenum, bismuth, iron, antimony and tellurium) on silica. Large quantities of hydrogen cyanide and acetonitrile by-products are formed in the reactor and also smaller quantities of acrolein, acetic acid, acrylic acid, propionitrile and methanocrylonitrile [57].

Due to the presence of impurities, it is impossible to recycle the ammonia and it must be removed with sulfuric acid [57]

An acrylonitrile plant also involves ammonium sulfate unit, recovery and purification sections [57].

## B-5.1.6 Ethylene Dichloride/Vinyl Chloride Monomer Production

Ethylene dichloride is mainly used for the production of vinyl chloride monomer, and vinyl chloride monomer is itself used almost exclusively in the manufacture of the commercially important plastic polyvinyl chloride and associated homo-polymers/co-polymers [68].

In the ethylene based process, ethylene dichloride (EDC) is synthesized by the chlorination of ethylene (direct chlorination) or by the chlorination of ethylene with hydrochloric acid and oxygen (oxychlorination). Thermal cracking of dry, pure ethylene dichloride then produces vinyl chloride monomer (VCM) and hydrochloric acid. When all the hydrochloric acid generated in EDC cracking is re-used in an oxychlorination section, and when no EDC or HCl is imported or exported, then the VCM unit is called a "balanced unit". By using both direct chlorination and oxychlorination for EDC production, balanced units achieve a high level of by-product utilization. The reactions are represented by the formulae [68]:

Chlorination: $C_2H_4 + Cl_2 \rightarrow C_2H_4Cl_2\{EDC\}$ Eqn (15)Cracking: $(CH_2Cl)_2 \rightarrow CH_2CHCl\{VCM\} + HCl$ Eqn (16)

Oxychlorination:  $C_2H_4 + \frac{1}{2}O_2 + 2HCl \rightarrow CH_2Cl_2\{EDC\} + H_2O$  Eqn (17)

Other operations in EDC/VCM production involve EDC purification, EDC cracking, VCM purification and storage [68].

B-5.1.7 PVC Production

PVC, polyvinyl chloride, is one of the three highest volume polymers, slightly behind polyethylene and polypropylene [68].

Generally, there are three different processes used in the manufacture of PVC [68]:

Suspension process: In the suspension PVC process, a suspension of PVC particles having a mean particle size of between 50 and 200 μm is produced.

Besides particle size, the essential differences between S-PVC grades result from the average length of polymer chains and from the porosity of the particles. Suspension PVC is always produced batch wise in a stirred vessel.

- Emulsion process: In emulsion processes, aqueous latex with the PVC having a mean particle size of between 0.1 to 3 micrometers is produced. Emulsion PVC is manufactured essentially by three polymerization processes: batch emulsion, continuous emulsion, and microsuspension. All these processes are used to produce a range of latex particle size distributions and thus plastisols rheologies.
- Mass (bulk) process:

# B-5.1.8 Polypropylene Production

Most of the processes applied for production of polypropylene are very similar to ones used to produce high density polyethylene. Generally, two different processes are applied in the production of polypropylene:

- Gas phase processes: In gas phase processes, gaseous polypropylene comes into contact with the solid catalyst which is intimately dispersed in dry polymer powder. Fluidized bed, vertical or horizontal reactors can be used in gas phase processes.
- Slurry phase processes: Propylene, diluent ( $C_6$  to  $C_{12}$  saturated hydrocarbons), hydrogen, catalyst and cocatalyst are continuously fed to the polymerization section, which normally consists of one or more stirred tank reactors in series. The polymerized polypropylene forms small powder particles suspended in the diluent. The slurry is continuously withdrawn from the last reactor after which unreacted polypropylene is removed from the slurry and recycled to the reactor. Next the polymer slurry is either treated in an alcohol and water wash system or fed directly to a slurry concentrating device from where the wet polymer powder is fed to a dryer. The treatment of polymer slurry depends on the type of catalyst used in the polymerization.

### B-5.1.9 Polystyrene Production

Polystyrene belongs to the group of standard thermoplastics that also includes polyethylene, polypropylene and polyvinyl chloride. In practice, three different types of polystyrene are distinguished. The transparent and brittle polymer is called general purpose polystyrene (GPPS), the white non-shiny but relatively flexible, rubber modified polystyrene is called (high) impact polystyrene (IPS or HIPS). Expandable or foam polystyrene (EPS) is the third group to distinguish due to its different production techniques [68].

The process of producing polystyrene requires one reactor or a series of reactors controlled by a set of parameters such as temperature, pressure and conversion rate. The process requires addition of several raw materials, i.e. solvent, initiator (optional), and chain transfer agent, into the reactors under well-defined conditions [68].

In general purpose polystyrene (GPPS) process, raw materials like styrene and processing aid are fed into the reactor(s). The reactor train usually includes continuous stirred tank reactors (CSTR) and/or plug flow reactors (PF). Additional chemicals are added into the feed stream or into the reactors. The process flow then goes through a devolatilisation section where it faces one or two flashes to separate the polymer from the unreacted species. Between two devolatilisation steps, an injection of water can be added to improve monomer removal. After condensation, unreacted styrene and ethyl benzene are recycled to the feed line, either directly using a recycle loop or through a storage tank. A purge of undesirable components is carried out with this stream [68].

High impact polystyrene (HIPS) process is very similar to the GPPS. The main difference is the addition of rubber component. The antioxidant is usually also added in the dissolving tank. In addition other chemicals can be added there such as white oil, peroxides, recycled styrene, ethylbenzene or chain transfer agents [68].

Suspension polymerization is still the mostly used process for large volume production of expandable polystyrene. Typically, styrene is dispersed under agitation in the aqueous phase containing some suspension agents and/or protective colloids and some secondary ingredients such as electrolytes. Both organic and mineral suspension agent systems can be used. Organic peroxides are added to styrene prior to its dispersion into water phase [68].

The polymerization then follows a schedule that raises the temperature of the reaction mixture stepwise towards nearly total conversion of the monomer into polymer. Pentane, a mixture of normal and isopentane, is added as a blowing agent during the course of polymerization. At the end of polymerization, the suspension is cooled; the expandable polystyrene beads are separated by centrifugation, washed and then dried at a relatively low temperature of 35°C. Following this, the beads are then screened into several bead size fractions corresponding to the various commercial needs and applications.

### B-5.1.10 Production of Styrene Butadiene Rubber

Styrene butadiene rubber has two types; namely emulsion polymerized styrene butadiene rubber and solution polymerized styrene butadiene rubber.

Emulsion polymerized styrene butadiene rubber (ESBR) production plants rely on readily available monomers, styrene and butadiene. A wide range of other chemicals such as emulsifiers, catalysts, modifiers, shortstops, antioxidants and extender oils are also required [68].

Above a critical concentration, surfactant molecules form aggregates called micelles. The addition of monomers which are insoluble in water, such as styrene or butadiene, to the stirred soap solution results in droplets of monomers stabilized by soap molecules being formed [68].

Despite being highly insoluble, the monomer is able to diffuse through the water to the soap micelles where it enters the hydrocarbon rich interior of the micelle. The addition of a free radical catalyst results in a polymerization reaction occurring within the micelle. The polymerization is fuelled by more monomer diffusing from the droplets to, what now is called the growing latex particle [68].

The molecular weight of the polymer molecules is regulated by the addition of a chain transfer agent or modifier. This has the effect of terminating one growing molecule and initiating another. The more modifier is added, the lower the molecular weight of the final product [68].

The reaction is carried out continuously is a series of continuously stirred tank reactors (CSTR) under moderate pressure. The latex is then stripped of unreacted monomers. Butadiene is removed in flash tanks, the first to atmospheric pressure and an optional second under vacuum. The latex then passes to steam stripping columns, where styrene is removed [68].

# B-5.1.11 Production of Polybutadiene Rubber

Typically a solution butadiene rubber process can be subdivided into the following process steps:

- Purification of monomers and solvent: solution processes often comprise an anionically catalyzed polymerization process. Purification is generally operated in a continuous mode. Recycled and make-up solvent is passed through a bed containing molecular sieves. Alternatively, packed alumina columns or distillation columns may be used.
- Polymerization: the polymerization reaction is carried out in a batch or in a continuous mode depending on the specific process. The reactor is charged with solvent and catalyst. Depending on the target polymer, monomers are added sequentially. Where a random copolymer is required, a structure modifier, usually an ether is added. Depending on target molecule, a coupling agent is added.
- Hydrogenation: for the production of hydrogenated solution rubbers, the polymer solution is introduced into a reactor. The reactor is able to be operated at elevated temperatures and pressures in order to allow fast hydrogenation. Commonly used catalysts are Ti and Ni species, sometimes in combination with aluminum alkyls.
- Blending section: the polymeric solution subsequently goes to a blending section comprising storage vessels of different sizes. Batches are blended following plant specific blending rules.
- Solvent removal and product isolation: there are to main techniques removal of solvent from the rubber solution; steam stripping and devolatilising extrusion. The criteria used for choosing either of these techniques depend primarily on the properties of the rubber and the customer's process requirements.
- o Packaging

#### **B-6.1** Power Stations

Energy generation by using fossil fuels involves burning in a furnace or combustion chamber of a boiler for steam production. Combustion can be defined as the rapid chemical combination of oxygen with the combustible elements of a fuel. In a boiler furnace (where no mechanical work is carried out), the heat energy derived from the reaction of combustible elements with oxygen depends on the ultimate products of combustion and not on any intermediate combinations that occur in reaching the final result [79].

Some different combustion techniques are given below [79]:

- **Pulverized solid fuel firing**: In more than 90% of the capacity of solid fuel combustion systems, the fuel is pulverized before combustion.
- Fluidized bed combustion furnace
- Grate firing
- **Oil and gas firing**: Gaseous fuel is directly combusted with air, whereas liquid fuels are sprayed into the furnace via nozzles, generating very small droplets atomized by high pressure steam and producing high amounts of volatiles.
- Gasification/ Liquifaction: Small gasification units operating at atmospheric pressure are often used for biomass. Liquifaction has been applied in refineries to produce secondary petrol for transport applications. For large power plants, gasification is more interesting under pressurized and high temperature conditions, as direct conversion of heat to electricity is possible in gas turbine and indirectly by steam turbines or combining both.

The direct expansion of hot pressurized gas in gas turbines and combustion engines allows the generation of mechanical and subsequently electrical energy [79].

Heat for the system is usually provided by the combustion of coal, natural gas, or oil. The fuel is pumped into the boiler's furnace. The boiler generates steam in the pressurized vessel in small boilers or in the water-wall tube system in modern utility and industrial boilers. High temperature, high pressure steam is generated in boiler and then enters the steam turbine. At the other end of the steam turbine is the condenser, which is kept at low temperature and pressure. Steam rushing from the high pressure boiler to the low pressure condenser drives the turbine blades, which power the electric generator [79].

Cooling is necessary to condensate the steam. In condenser located downstream of the low pressure section of the turbine, steam is condensed back to water (condensate) [79].

Gas turbine systems operate in a manner similar to steam turbine systems except that combustion gases are used to turn the turbine blades instead of steam. Unlike a steam turbine system, gas turbine systems do not have boilers or a steam supply, condensers or a waste heat disposal system [79].

So-called condensing power plants use ambient cooling sources to condense the steam at the lowest available temperature and under vacuum conditions [79].

The major types of fossil fuels that can be used for electricity generation include coal, lignite, petroleum, gas, petroleum coke, refinery gas, coke oven gas, blast furnace gas and liquefied petroleum gas [77].

Coals used for electric power generation are very heterogeneous and vary in content, dependent on the location of mine. The major chemical makeup which includes carbon, hydrogen and oxygen, also contains impurities, such as minerals and sulfur. These impurities are a major concern because they contribute to pollutants produced during combustion of fuel. Petroleum, or crude oil, is the source of various fuel oils used as the energy source for power generation. Typical fuel oils include fuel oil numbers, 4, 5, and 6 (heavy oil) and constitute the majority of all petroleum receipts at electric utilities. Gas is used less than coal as a primary fuel source at power generation utilities; however, it is widely used for industrial electric power generation. Gas has one advantage over other fuels in that it is a cleaner burning fuel [77].

Sulfur oxides are emitted from the combustion of most fossil fuels through oxidation of the sulfur contained in the fuel. Primary measures to reduce sulfur oxide emissions include use of low sulfur fuel or fuel with basic ash compounds for internal desulfurization, use of adsorbent in fluidized bed combustion systems. Secondary measures include flue gas desulfurization units.

Wet scrubbers, especially the limestone-gypsum processes, are the leading FGD technologies due to their high  $SO_2$  removal efficiency and their reliability. Limestone is used in most cases as the sorbent, as it is always available in large quantities in many countries and is cheaper to process than other sorbents [79].

The flue gas leaving the particulate control system usually passes through a heat exchanger and enters the FGD absorber, in which  $SO_2$  is removed by direct contact with an aqueous suspension of finely ground limestone whereas limestone should have more than 95% of CaCO<sub>3</sub>. Fresh limestone slurry is continuously charged into absorber. The scrubbed flue-gas passes through the mist eliminator and is emitted to the atmosphere from a stack or cooling tower. Reaction products are withdrawn from the absorber and are sent for dewatering and further processing [79]. The wet limestone scrubber is generally divided into two categories according to the type of oxidation: forced oxidation or natural oxidation mode. By-products are either gypsum or mixture of calcium sulfate/sulfite, depending on the oxidation mode [79].

B-6.2 Aluminum Thermal Metallurgy

#### Primary Aluminum Process

Primary aluminum is produced from bauxite that is converted into alumina. 100 tons of bauxite produces 40 - 50 tons of alumina (aluminum oxide) which then produces 20 - 25 tons of aluminum [78].

Alumina is produced from bauxite in the well-established Bayer process given in Figure B-6.1.



Figure B-6. 1 Bayer process [78]

The overall process is standard for all sites and uses caustic soda to extract alumina from bauxite at elevated temperatures and pressures in digesters. Slurry is produced, which contains dissolved sodium aluminate and a mixture of metal oxides called red mud that is removed in thickeners. The aluminate solution is cooled and seeded with alumina to crystallize hydrated alumina. The crystals are washed and then calcined in rotary kilns or fluid bed/fluid flash calciners before use or shipping. Other metals such as vanadium may be present and can also be recovered from the liquor [78].

Aluminum is produced from primary materials by the electrolytic reduction of aluminum oxide (alumina) dissolved in a molten bath of mainly sodium aluminum fluoride (cryolite). The electrolytic cells comprise a carbon cathode, insulated by refractory bricks inside a rectangular steel shell, and a carbon anode suspended from an electrically conductive anode beam. Liquid aluminum is deposited at the cathode in the bottom of the cell and oxygen combines with the carbon anode, to form carbon dioxide. The carbon anodes are therefore continuously consumed during the process [78].

Alumina is added to the cells to maintain an alumina content of 2 - 6% in the molten bath. Fluoride compounds are added to lower the bath melting point, enabling the cells to be operated at a lower temperature. Aluminum fluoride (AIF<sub>3</sub>), the most common additive, also neutralizes the sodium oxide present as an impurity in the alumina feed [78].

The cathode is not consumed in the process but the cathodes deteriorate with time. Carbon blocks absorb electrolyte and after 5 - 8 years have to be replaced due to swelling and cracking which results in penetration of molten electrolyte and aluminum to the cathode conductor bar and steel shell. Small amounts of cyanides are formed through a reaction between nitrogen and carbon. The cathode residue is known as spent pot lining, several disposal and recycling routes for this material are used [78].

Molten aluminum is periodically withdrawn from the cells by vacuum siphon and is transported to the casting plant and the aluminum emptied into heated holding furnaces. Alloying additions are made in these furnaces. Skimmings formed by the oxidation of molten aluminum on the surface of the melt are skimmed off [78].

The metal is refined at this stage to remove impurities such as sodium, magnesium, calcium oxide particles and hydrogen. This refining stage is performed by the injection of a gas into the molten metal usually in an in-line reactor. The treatment gas used varies depending on the impurities. Skimmings are produced at this stage and are removed from the surface of the molten metal and are recycled by the secondary aluminum industry [78].

# Secondary Aluminum Process

The secondary industry is dependent on sources of scrap. Scrap can be termed "New Scrap" that is generated during the production and fabrication of wrought and cast products or "Old Scrap" that is recovered from articles at the end of their useful life [78].

Typical sources of aluminum scrap are process scrap, used beverage cans (UBCs), foils, extrusions, commercial scraps, turnings, and old rolled or cast metal. In

addition to this aluminum is also recovered from skimmings and salt slags Scraps such as UBCs and turnings may be contaminated [78].

The main feature of secondary aluminum production is the diversity of raw materials encountered and the variety of furnaces used. The type of raw material and its pre-treatment is therefore used to judge the best type of furnace to be used for a particular type of scrap with its size, oxide content and degree of contamination among others [78].

Rotary or reverberatory furnaces are used for melting a wide range of secondary raw materials, rotary furnaces can incorporate a tilting mechanism and this is reported to reduce the amount of flux needed. Induction furnaces and the Meltower process are used to melt the cleaner aluminum grades [78].

Secondary aluminum process is given in Figure B-6.2.



Figure B-6. 2 Secondary aluminum process [78]

Metal may be tapped from the melting furnace where alloy additions are made either directly to a casting system or via a transfer system into a holding furnace (where other alloying additions can be made). The metal is then refined either in the holding
furnace or in an inline reactor, to remove gases and other metals generally in the same manner as primary aluminum [78].

Cold skimmings are treated by a number processes to recover aluminum. Rotary furnaces are used to recover aluminum from skimmings and the metallic fraction produced from the treatment of skimmings [78].

The large blocks of salt slag are crushed to manageable size and sieved to recover metallic aluminum granules (typically up to 10%). The finely crushed material is then dissolved in water so that the chlorides go into solution producing brine, leaving the insoluble aluminum oxide and the finest metallic particles of aluminum, which is not normally economically recyclable as the metal [78].

# B-6.3 Lead Thermal Metallurgy

Refined lead is derived from primary material in the form of lead ores and concentrates, and secondary material in the form of scrap and residue.

# Primary Lead Process

There are two basic pyrometallurgical processes available for the production of lead from lead sulfide or mixed lead and zinc sulfide concentrates: - sintering/smelting or direct smelting. The processes may also be used for concentrates mixed with secondary raw materials [78].

Lead concentrates are blended with recycled sinter fines, secondary material and other process materials and pelletized in rotating drums. Pellets are fed onto an up draught or down draught sinter machine and ignited. The burning pellets are conveyed over a series of wind-boxes through which air is blown. Sulfur is oxidized to sulfur dioxide and the reaction generates enough heat to fuse and agglomerate the pellets [78].

The sulfur dioxide is recovered from the sinter machine off-gases, which are cooled, cleaned and recovered in the form of sulfuric acid. Cadmium and mercury are also present and are recovered from the off-gases or from the sulfuric acid that is produced [78].

Sinter is charged to the blast furnace with metallurgical coke. This generates sufficient heat to melt the charge. The gangue content of the furnace charge combines

with the added fluxes or reagents to form a slag [78]. The carbon monoxide reduces the metal oxides in the charge. Slag and lead collect in the furnace bottom and are tapped out periodically or continuously [78].

For smelting bulk lead and zinc concentrates and secondary material, a specially designed blast furnace called the Imperial Smelting Furnace is used. Here, hot sinter and pre-heated coke as well as hot briquettes are charged. Hot air, sometimes oxygen enriched is injected with these raw materials. The reduction of the metal oxides not only produces lead and slag but also zinc, which is volatile at the furnace operating temperature and passes out of the ISF with the furnace off-gases [78].

The furnace gases pass through a splash condenser in which a shower of molten lead quenches them and the metals are absorbed into the liquid lead. The resulting alloy is cooled when zinc floats to the surface and is separated from the lead. The zinc is refined by distillation. Lead is recycled to the splash condenser [78]. Imperial Smelting Process for lead and zinc production is given in Figure B-6.3.



Figure B-6. 3 Imperial Smelting Process[78]

Several processes are used for direct smelting of lead concentrates and some secondary material to produce crude lead and slag. Bath smelting processes are used – the ISA Smelt/Ausmelt furnaces (sometimes in combination with blast furnaces), Kaldo (TBRC) and QSL integrated processes are used in EU and Worldwide [78].

The sintering stage is not carried out separately in direct smelting. Lead sulfide concentrates and secondary materials are charged directly to a furnace and are then melted and oxidized. Sulfur dioxide is formed and is collected, cleaned and converted to sulfuric acid. Carbon (coke or gas) and fluxing agents are added to the molten charge and lead oxide is reduced to lead, a slag is formed. Some zinc and cadmium are "fumed" off in the furnace, their oxides are captured in the abatement plant and recovered [78].

# Secondary Lead Process

Scrap automotive batteries (automotive, motive power and stand by) are a major source of secondary lead [78].

There are two main types of process for the recovery of lead from automotive batteries:-

Batteries are drained of acid and fed whole into a blast or shaft furnace (Varta process) or whole batteries and fluxes are fed into a blast furnace via a seal and oxygen enriched air is used in the blast. Antimonial lead bullion is produced, along with a silica based slag and a lead/iron matte that can be recovered in a primary lead smelter

Organic components in the furnace off-gases are oxidized in an after- burner and the gases are then cooled and filtered in a fabric filter. The filter dust is dechlorinated and returned to the furnace [78].

Batteries are drained of acid broken and separated into various fractions using automated proprietary equipment (MA and CX processes). Both the MA and CX (Engitec) processes use hammer type mills to crush the whole batteries. The crushed material then passes through a series of screens, wet classifiers and filters to obtain separate fractions containing metallic components, lead oxidesulfate paste, polypropylene, non recyclable plastics and rubber and dilute sulfuric acid. Some processes use a second milling stage before the plastic

fraction is finally treated. Polypropylene is recycled as far as possible. The sulfuric acid drained from the batteries is neutralized unless there is a local use for it and the sodium sulfate produced can be re-crystallized and sold. These are strongly market dependent options [78]

A second way for secondary production of lead is recovery from other scraps and residues. Metallic lead scrap may be in a variety of forms, it may be contaminated by plastic material or bitumen and may be alloyed with other elements, notably tin, antimony and silver. Recovery from scrap and residues are done by a similar process to recovery of lead from scrap batteries. The electric furnace is also used for the recovery of lead from complex lead/copper and lead/precious metals secondary materials [78].

Clean scrap is melted in specially designed kettles, which are indirectly heated by oil or gas. Dross and tramp materials are skimmed from the surface of the molten metal and then pass through a screen that separates fine and coarse fractions. The dross is the fine fraction and is recycled as a non-metallic residue. The tramp material is mostly metal with a higher melting point than lead, and is treated elsewhere [78].

If necessary the lead or lead alloy recovered from scrap can be refined to remove copper, bismuth, antimony, arsenic and tin. A pyrometallurgical refinery consists of a series of kettles, which are indirectly heated by oil or gas. Copper is the first element to be removed and separates as sulfide dross. Arsenic, antimony and tin are removed by oxidation. The usual method, often referred to as "lead softening", involves a reaction with a mixture of sodium nitrate and caustic soda, followed by mechanical skimming to remove the oxide dross. De-silvering is carried out by the Parkes process, which makes use of the preferential solubility of silver in zinc. Bismuth is removed by treatment with a mixture of calcium and magnesium (the Kroll-Betterton process). A calcium-magnesium-bismuth alloy is formed as dross on the surface of the lead and is removed by skimming. The dross is then oxidized using lead chloride, chlorine gas or a caustic soda / sodium nitrate mixture and the calcium magnesium oxide is removed skimming [78].

# B-6.4 Copper Thermal Metallurgy

Primary copper may be produced from primary concentrates and other materials by pyrometallurgical or hydrometallurgical routes [78].

## Primary Pyrometallurgical Processes

#### o <u>Concentrate to matte smelting</u>

Partial roasting converts the complex sulfides of iron and copper in the concentrate into the simple sulfides by heating the ore or concentrate under oxidizing conditions. The sulfur based gases generated by this process are directed to on-site acid plants to be used as a raw material in the production of sulfuric acid or the production of liquid SO<sub>2</sub>. The smelting stage is then used to separate the copper sulfide from the other solids present in ores by the formation of silicates particularly iron silicates [78].

Roasting and smelting are usually carried out simultaneously in a single furnace at high temperatures to produce a melt that can be separated into a matte (copper sulfide with some iron sulfide) and a slag rich in iron and silica [78].

There are two basic smelting processes in use, bath smelting and flash smelting. All of the processes rely on the roasting and smelting processes taking place in a molten bath with slag and matte separation and tapping taking place in various ways [78].

o <u>Converting</u>

Two types of converter processes are used namely; batch and continuous converting [78].

The batch converting process comprises two stages. It is carried out by blowing an air/oxygen mixture through the matte recovered from the smelting operation. In the first stage iron and part of the sulfur are oxidized and slag and sulfur dioxide gas are formed; the slag is skimmed off periodically and is further processed to recover copper. The sulfur dioxide that is formed is further treated for sulfur recovery, normally in a sulfuric acid plant [78].

The continuous converting processes that are in industrial use are the Kennecott / Outokumpu flash converting furnace, the Mitsubishi furnace (which forms part of the integrated Mitsubishi process) and – very recently - the Noranda converter. The Mitsubishi and the Noranda converters receive molten feed for conversion. In contrast the Kennecott / Outokumpu process has the following features: - Matte from a smelting furnace is first granulated in water, crushed and dried. The material is then blended

with slagging agents and fed into the concentrate burner of a specific flash furnace using an oxygen rich atmosphere; conversion takes place in the air borne particles. Slag and blister copper are tapped for further processing [78].

## o Fire refining

This is a further purification step applied to the crude metal (blister copper) produced by the conversion stage. The refining step involves the addition of air and then a reductant (e.g. hydrocarbons etc) to reduce any oxide present [78].

## • <u>Electrolytic refining</u>

An electrolytic cell is used consisting of a cast copper anode and a cathode, placed in an electrolyte containing copper sulfate and sulfuric acid. The cathode is either a thin blank of pure copper (starter sheet) or a stainless steel former sheet – permanent cathode plate. At high current density and low voltage, copper ions are dissolved from the impure anode and pass into solution from where they are deposited onto the cathode. The remaining anode is then recycled to the production process, usually the converter, to cool the reaction and recover the copper [78].

#### o <u>Slag treatment</u>

The slags produced from the primary smelting with high matte grades and converting stages are rich in copper and are subjected to a number of slag treatment processes. One process is the use of an electric furnace for the reaction of slag with carbon in the form of coke breeze or the electrodes themselves and for the settling of copper matte that is formed to produce an inert slag. Converter slag can also be returned directly to the electric slag-cleaning furnace or to the smelting furnace. Alternatively, flotation processes are also used after the slag has been slow cooled, crushed and milled, the flotation concentrate obtained is a copper rich portion and is returned to the smelter [78].

Slags from the slag treatment processes may be reused [78].

Other slags rich in copper like the refining slag are normally re-circulated to a prior process stage, mostly converting, or, in secondary smelters, to the smelting stage [78].

#### Secondary Production Processes

Secondary copper is produced by pyrometallurgical processes [78]. For secondary smelting processes, a number of furnaces such as the Blast, Mini Smelter, Top Blown Rotary Furnaces (TBRC), Sealed Submerged Arc Electric Furnace, ISA Smelt, Reverberatory, and Rotary are used for low and medium grade material. The type of furnace and the process steps used depends on the copper content of the secondary raw material, its size and other constituents [78].

Converting and refining furnaces are very similar to those used for primary production and the slag treatment systems and electro-refining processes are the same. The main difference is that converters used for secondary production treat metal and not matte. Secondary converters also oxidize and slag minor elements like iron and separate other metals like zinc or tin by volatilization. Fire refining furnaces are used also to melt higher grade scrap [78].

Copper alloys such as bronzes and brasses are also used as secondary raw materials in a number of processes [78].

### **B-7 Surface Treatment and Coating of Metals**

The surface properties of metals are typically changed for:

- o Decoration and/or reflectivity
- o Improved hardness
- Prevention of corrosion [81]

The surface properties of plastics are changed for:

- $\circ$  Decoration
- o Reflectivity
- Durability
- Electrical conductivity [81]

These requirements are met by depositing layers of metals on the surface of the plastic [81].

Despite the complexity and the range of activities all workpieces or substrates pass along a common route of activities. The first activity on site is delivery and storage of incoming workpieces, substrates and raw materials. Workpieces or components are loaded onto appropriate transport systems prior to pretreatment, such as degreasing. Most workpieces or components are given more than one pretreatment and some of these may be prior to loading to a process line. Among mechanical pretreatment linishing and polishing, abrasive blasting, deburring and/or tumbling can be used [81].

Mechanical polishing produces a flowed amorphous surface under the influence of pressure and high local temperature. Abrasive blasting may be used to de-stress the surface of the workpieces. As well as the mechanical methods, electrolytic and chemical processes are employed in the production of smooth, bright surfaces [81].

Electropolishing is a commonly used electrochemical method for smoothing, polishing, deburring and cleaning various metals, generally steel, copper and its alloys and aluminum and its aluminum alloys [81].

Solvent degreasing is usually by means of chlorinated hydrocarbons, alcohols, terpenes, ketones, mineral spirits hydrocarbons. There are two types of process:

- Cold cleaning: The workpieces or substrates are immersed in the solvent or cleaned in a stream of solvent.
- Vapor phase: The solvent is vaporized in a purpose-built bath and the cold component suspended in the vapor [81].

In aqueous cleaning the workpieces are placed in a solution or placed in a spray bath. The solution is alkaline or neutral but may be acidic and usually working at increased temperatures. The main components of the aqueous cleaning systems are alkalis or acids, silicates, phosphates and complexing and wetting agents Other cleaning systems include air knives which are used to remove excess oil and grease from parts, centrifuges, dry ice and hand wiping [81].

Pickling and desalting are chemical metal-stripping procedures used to brighten and/or remove oxides from the degreased metallic surface prior to other surface treatment processes. During the pickling processes distributed or adhering layers, such as scale, oxide films and other corrosion products of the metal, are removed by chemical reaction with an acid-based pickling agent. Hydrochloric and sulfuric acids are used [81].

Metal stripping is necessary for the processing of defectively electroplated components without losing the properties of the base material [81].

Pretreatment is essential in the surface treatment of plastics by autocatalytic plating and printed circuit boards. Conditioning of plastics provides wetability of the surface as a prerequisite for subsequent voidless covering and good adhesion of metal layers. The process solution contains sulfuric acid or sodium hydroxide and carbonate, water soluble organic biodegradable solvents. The picking of plastic is a prerequisite for good metal adhesion. It is carried out in an aqueous mixture of chromic acid, sulfuric acid and wetting agent.

Rinsing is usually carried out between process steps, whether they are pretreatment and/or core processing steps. Drag-out is the liquid from the previous process which adheres to the workpieces or substrate surfaces which necessitates rinsing;

• Between most process steps to prevent cross-contamination of process solutions

To ensure there is no deterioration of the workpieces and/or substrate surface by residual chemicals, such s by over-reaction or by staining by the drying of dissolved chemicals [81].

Treatment is followed by after treatments such as drying, and the workpieces or substrates are stored and dispatched. Substrates may be dried using hot water, hot air or air knives. [81].

Core activities of surface treatment of metals and plastics are given below.

B-7.1 Copper and Copper Alloy Plating

Cyanide copper low temperature electrolytes are necessary for strike plating on steel and zinc die casts to prevent spontaneous cementation of copper and poor adhesion of the subsequent metal deposit. This type of solution is based on copper cyanide and sodium cyanide [81].

Acid copper electrolytes based on copper sulfate and sulfuric acid are used to make polishing and buffing redundant prior to decorative bright nickel and copper plating on furniture frames, bathroom fittings, wire work etc [81].

Autocatalytic copper plating is still a key process in printed circuit boards and as well as for the metallization of plastics. Plastics require etching before deposition. Copper deposition starts on metal nuclei such as palladium and continues autocatalytically [81].

Brass is predominantly an alloy of copper and zinc although nickel, tin or lead may be added. A mixture of copper and zinc cyanides in solution are widely used to deposit copper and zinc alloys for decorative purposes [81].

Bronze is copper alloy with tin and zinc. Cyanide bronze alloy is used as a decorative plating process [81].

B-7.2 Nickel Electroplating

Nickel plating processes- including both electrolytic and electroless systemscan conveniently be considered in seven separate categories.

- *Nickel/chromium electroplating*: It is the most important application of nickel and also called chrome plating.
- *Nickel electroplating with other topcoats*: Brass, gold and silver topcoat systems are used as alternatives to chromium.
- Nickel electroplating: Nickel can be used on its own without any topcoat.
- Nickel composite electroplating systems: Nickel matrixes can be formed in which inert non-metallic particles, such as silicon carbide, diamond or PTFE are incorporated by co-deposition to improve engineering properties such as hardness.
- *Nickel alloy electroplating*: Electrodeposited nickel alloys of commercial significance include zinc-nickel, nickel-cobalt, and nickel-iron.
- *Nickel electroforming*: This process which is a vital part of manufacturing compact discs and DVDs allows articles to be produced by the electrodeposition of relatively thick nickel layers.
- *Electroless nickel plating*: This is a chemical process giving hard uniform coatings. It is also called autocatalytic plating. [81]

Watts-type nickel solutions account for the majority of solutions used in the nickel plating industry, including those used for nickel-chromium plating, nickel with other topcoat systems and composite nickel plating. Nickel sulfamate- based solutions

are widely used and most frequently in electroforming applications. They are also used in barrel plating operations and reel-to-reel. The solutions are based on nickel sulfamate rather than nickel sulfate. Solutions based on nickel chloride have very limited uses due to the very high internal stresses of deposits they produce. Solutions based on nickel sulfate and not containing nickel chloride are rarely used as they do not promote good dissolution of the nickel anode material. As nickel alloy plating solutions Watts-type or nickel sulfamate formulations can be used [81].

Similar to autocatalytic copper, electroless nickel solutions are used for generating a first conductive metal layer on plastic surfaces prior to further electrolytic metal deposition. Plastics require etching before deposition [81].

# B-7.3 Chromium Plating

Bright hexavalent chromium plating electrolytes are based on chromic acid, sulfate as the primary catalyst such as fluoride ions. Bright trivalent chromium electroplating electrolytes are based on the chromium III compounds, such as sulfate or chloride together with proprietary chemicals. Black chromium finishes can be achieved for decorative black pieces and on the same substrates as for bright chromium plating. They are based on hexavalent chromic acid electrolytes and catalysts (nitrates, fluorides). Hard chromium plating electrolytes are based on chromic acid and either of sulfate ions, mixed sulfate and fluoride ions and pre-prepared proprietary fluoride-free as a catalyst [81].

# B-7.4 Zinc and Alloy Plating

Alkaline cyanide zinc is used mainly for technical corrosion-resistant layers. Electrolytes have compositions of zinc oxide, sodium hydroxide and sodium cyanide. Alkaline cyanide-free zinc electrolytes are mainly applied for technical corrosionresistant layers. The process solutions contain zinc oxide and sodium hydroxide or potassium hydroxide. Acid zinc electrolytes give bright decorative layers. Electrolytes contain zinc chloride, potassium and/or sodium chloride, boric acid and wetting agent. The main zinc alloys deposited are:

• Zinc/iron from alkaline cyanide-free electrolytes

- Zinc-cobalt from acid or alkaline cyanide-free electrolytes
- Zinc-nickel from acid or alkaline cyanide-free electrolytes [81].

## B-7.5 Cadmium plating

Cadmium is mainly used to protect parts made of steel and aluminum or titanium alloys. Cadmium plating can be performed in acidic as well as alkaline baths. Electrolytes may be based on cyanide, fluoroborate, sulfate and chloride [81].

### B-7.6 Tin and Alloy Plating

Several different electrolytes are available, such as acid stannous sulfate, acid tin fluoroborate, alkaline sodium or potassium stannate and more recently stannous systems based on organic acids such as methane, sulfonic acid [81].

#### B-7.7 Precious metal plating

Bright silver deposits are widely used for jewellery as well as on ornaments, trophies, giftware, etc. Due to its high conductivity and mechanical and chemical properties, silver layers are found on many components of electrical and electronic devices. The majority of silver electrolytes are based on potassium-silver cyanide [81].

Gold can be plated using rack, barrel or high speed equipment either as a very pure metal or as an alloy. It finds use in a wide range of industries such as connectors, printed circuit boards, integrated circuits, giftware, buttons, watches etc. the majority of gold plating solutions in commercial plating facilities, whether the deposit has a decorative or functional requirement are based on mildly acid solutions of gold potassium cyanide as potassium cyanoaurate,  $KAu(CN)_2$  [81].

B-7.8 Immersion or displacement coatings- non-catalytic chemically reduced coatings

Non-catalytic chemically reduced coatings are formed when the metal to be deposited is precipitated on its reduction in solution either chemically from solution or the metallic substrate is more active than the ions in the solution in terms of the electromotive or electrochemical series [81].

## B-7.9 Electroplating or Electrocoating

It is used to apply a protective coating after decorative finishes and as an alternative or supplement to corrosion-prevention layers, such as replacing hexavalent chromium conversion coatings on its own or used in conjunction with trivalent chromium systems [81].

#### **B-7.10** Lacquering

Lacquers are applied to protect and enhance decorative coatings or to supplement corrosion protection systems such as chromating. They also reduce friction and enable parts to be evenly or readily distributed without surface damage. They can be applied by dipping in a proprietary water-based solution or by electropainting [81].

## B-7.11 Anodizing

The anodizing of metals is an electrolytic surface oxidation process which enhances the natural aptitude for the metal to oxidize. Aluminum is the most important material to be anodized by using sulfuric acid and chromic acid, with alumina  $(Al_2O_3)$  formed at the surface. Aluminum can be colored in many shades and colors in conjunction or after sulfuric acid anodizing and is normally referred to as color anodizing [81].

Phosphoric acid anodizing is being increasingly used as a preparative treatment for subsequent applications of organic or plated coatings. [81]. Sulfuric acid anodizing is normally followed by a sealing process [81].

## B-7.12 Phosphating layer conversion coatings

They are used to treat steel, aluminum and zinc for cold forming, coil coating, rust proofing, bearing surface lubrication, paint base, electrical insulation [81].

Zinc phosphating is primarily used for the surface treatment of steel and zinc as well as composite of these metals with aluminum. Essential constituents are zinc, phosphate ions and an oxidizing agent [81].

#### B-7.13 Chromium Conversion Coating

Chromium conversion coatings are used to enhance corrosion protection on various metal surface, including electroplated zinc and cadmium, zinc die castings, tin, aluminum, magnesium and magnesium alloys, copper, brass and bronze, nickel, silver and stainless steel. Conventional processes are all based on the use of acid oxidizing solutions, the oxidant being hexavalent chromium (Cr(VI)). Trivalent chromium (Cr (III)) conversion coating processes do not contain hexavalent chromium [81].

# B-7.14 Chemical blacking-oxide coatings

Steel may be blackened in high temperature bath containing sodium hydroxide and sodium nitrate. Stainless steel can also be blackened in molten sodium/potassium dichromate at high temperatures. Copper may be blackened in a bath containing a mixture of sodium hydroxide and sodium chlorite. Brass may be blackened in the same solution but may not respond, depending on the zinc content and metallurgical history [81].

# **B-7.15** Brightening

Copper and brass are brightened by oxidizing a surface layer. Aluminum and some of its alloys can be brightened by chemical or electrochemical processes for special applications such as lighting and decorative finishes [81].

# B-7.16 Etching-Alkaline Etching of Aluminum

The most frequently used method for etching aluminum is aqueous solutions of caustic soda, with or without other additives [81].

B-7.17 Chemical Milling

Chemical milling is a process used to remove metal on workpieces by dissolution in a caustic or acid bath without an external source of energy (mechanical or electrical).

## **B-8: Organic Solvents**

Organic solvents are described as any Volatile Organic Compounds (VOC) which is used alone or in combination with other agents, and without undergoing a chemical change, to dissolve raw materials, products or waste materials, or is used as a cleaning agent to dissolve contaminants, or as a dissolver, or as a dispersion medium, or as a viscosity adjuster, or as a surface tension adjuster, or a plasticizer, or as a preservative [95]. Moreover, halogenated solvents are described as an organic solvent which contains at least one atom of bromine, chlorine, fluorine or iodine per molecule [85].

According to the COUNCIL DIRECTIVE 1999/13/EC the activities in which solvents are used are listed as follows:

- o Adhesive coating
- Coating activity in which a single or multiple application of a continuous film of coating is applied to vehicles (new cars, truck cabins, vans and trucks and busses etc.), trailers, metallic and plastic surfaces, wooden surfaces, textile, fabric, film and paper surfaces and leather.
- Coil coating where coiled steel, stainless steel, coated steel, copper alloys or aluminum strips is coated with either a film forming or laminate coating in a continuous process.
- Dry cleaning
- Footwear manufacture
- o Manufacturing of coating preparations, varnishes, inks and adhesives
- o Manufacture of pharmaceutical products
- Printing in which, with the use of an image carrier, ink is transferred onto whatever type of surface (flexography, heatset web offset, laminating associated to a printing activity, publication rotogravure, rotogravure, rotary screen printing, varnishing).

- Rubber conversion
- Surface cleaning
- o Vegetable oil and animal fat extraction and vegetable oil refining activities
- Vehicle refinishing
- Winding wire coating
- Wood impregnation
- Wood and plastic lamination [81]

# B-8.1 Dry Cleaning Processes

Dry cleaning, processes garments in a way that avoids saturating fabrics with water. If thoroughly saturated with water, agitated and heated, certain fabrics (especially wool, silk and rayon) may shrink or the dye may run. Other garments that are constructed from several materials can be damaged if the various layers react differently to the cleaning process. Because dry cleaning solvents do not saturate the fibers of the fabric, the swelling and shrinking from water saturation is avoided [85].

Four solvents dominate the dry cleaning market: perchloroethylene (PCE), petroleum solvents, chlorofluorocarbons (CFC-113) and trichloroethane (TCA). The manufacture of latter two is banned in United States in 1995 under the Clean Air Act Amendments. Today PCE dominates the commercial sector [85].

The first generation of dry cleaning machines had separate washers and dryers [85].

Dry-to-dry machines, integrate the washing and drying into the same unit. Second generation machines can be retrofitted with control devices such as carbon adsorbers (not allowed under current regulations) and refrigerated condensers. Carbon adsorbers recover solvent by sending contaminated air through a bed of activated carbon that then adsorbs the solvent vapors. Refrigerated condensers remove vapors from the exhaust stream by cooling them to below their dew points. Refrigerated condensers achieve about 95 percent control of hazardous air pollutants (HAPs) when compared to uncontrolled machines [85].

The third generation of machines are closed loop machines. A closed-loop machine does not vent air to the atmosphere but recycles it continuously throughout the

dry cleaning cycle. The principles of operation are the same as for the second generation machines that use refrigerated condensers [85].

The fourth generation machine is a non-vented, closed loop process with an additional internal vapor recovery device. The control technologies used in these machines are refrigerated condensers and carbon adsorbers [85].

### **B-8.2** Printing Processes

Overview of main printing processes is given in Figure 1.

In different types of prints different types of printing processes are used. Newspapers are usually long runs printed on reels of uncoated paper. Practically all newspapers are printed by coldset web offset [88].

Magazines with a circulation over 10 000 are generally printed by heatset web offset, although shorter runs will be done by sheetfed web offset. Heatset web offset is also used to print travel brochures, mail order catalogues, and advertising material for inserting into newspapers and magazines. Very long run magazines and similar publications tend to be printed by gravure [88].

• Pre-press and proofing

Pre-press processes include text and image processing. The imaging process begins with composition and typesetting. Composition involves the arrangement of text, pictures and diagrams into the desired format. Once desired format and images are assembled, the data can be transferred in on a photographic film or digitally. Today, proofs can be made directly from the data in the computer being shown on the screen, or being printed out with an ink jet or laser print. Organic solvents are not used in the pre-press process [88].

## • Making image carrier

The image carriers (or printing plates) are used in the printing processes to transfer the printing ink onto the substrate (paper, cardboard, plastics etc.).



Figure B-8. 1 Main printing processes [88]

They are normally made by copying the films onto light-sensitive coatings on the printing plates, cylinders or screens, respectively. Before this, the film has to be mounted so that they correspond to the size of printing form and the printing sheet or web. New technology known as computer-to-plate (CTP) makes it possible to produce printing forms directly from computer without the photomechanical processes and the photographic films are no longer needed [88].

- Printing
  - a. Relief Printing

This uses a printing surface that is in relief, i.e. raised above the non-printing surface. Letterpress and letterset are as flexography relied printing methods, where the image is raised compared with the then non-printing areas. Nowadays plastic relief plates are used which is obtained by exposure of a negative film to light, the light hardening the plate in the image areas and the unhardened areas being processed. Letterset is an indirect flexographic printing process. The image is transferred to a rubber blanket (as in offset) and then onto the object to be printed [88].

Flexography which has now become the dominant relief printing process employs direct rotary printing using resilient relief plates such as rubber or, photopolymers and fast-drying solvent or water-based inks. The printing unit of the flexographic press consists of four main parts:

- Inking unit
- Ink-metering roll
- Plate cylinder
- Impression cylinder

The flexographic printing press can be either web- or sheetfed [88].

## b. Planographic printing

Lithography, usually abbreviated to litho, is where the image and non-image areas are in the sane plane on a plate, which can be of metal, plastic or paper. Because lithographic plates do not last when being constantly abraded by contact with the printing substrate on long print runs, the image is put or offset onto a softer intermediate blanket which transfers the image to the substrate. This type of printing is known as offset or offset litho and is the most commonly used process. In waterless litho non-printing areas use an ink repelling substance such as silicon. The substrate can be fed as a roll or web, known as webfed or as sheets (sheetfed). Heatset and coldset refers to the technique used to dry ink. Coldset is used mainly for newspapers and business forms, printed on absorbent uncoated papers, with no solvent emission from the inks. Inks used for heatset web work are dried by using ovens to drive off the solvent from the ink, resulting in emissions to air [88].

### c. Intaglio printing

In intaglio printing the printing areas are tiny recesses inscribed on a cylinder below the non-printing areas. The recesses are filled with ink, the surplus ink is removed and the substrate is pressed against the printing cylinder. An example is gravure. In gravure inks are low in viscosity and nearly all of them are solvent-based. Publication printing inks contain 50% toluene when leaving the ink factory. A dilution is made in the printing plant to obtain the proper concentration in toluene: ink that ready for use contains 70 - 80% toluene. These solvents are evaporated by heat and air in drying sections. Installations of publication gravure are generally equipped with an activated carbon adsorber to recover the toluene that is evaporated [88].

#### d. Stencil

In stencil printing such as screen printing the printing and non-printing areas are carried on a screen. The non-printing parts are formed by blocking out parts of the screen, while the ink is forced through the non-locked parts onto the substrate. A whole range of inks are used to match the great variety of end products in screen printing. Inks containing solvents dry by solvent evaporation, oxidation or catalysis. The selection of solvents is determined by the binder, substrate and method of drying. Typical solvents are aromatic and aliphatic hydrocarbons, glycol esters and esters, alcohols and ketones. Cleaning processes in screen printing include residual ink removal, cleaning out the ink, cleaning out the stencil, haze removal and degreasing [88].

# e. Digital

It produces an image directly onto a substrate from digital information without the creation of an intermediate permanent image. Normally the inks are solvent based containing volatile solvents such as methyl ethyl ketone, ethyl and butyl lactate [88].

#### • Finishing

The most important print finishing services include the processing of:

- o Books by folding, collecting stitching, binding an trimming
- Magazines, leaflets, catalogues and printed advertising products by folding gathering, gluing and perfect binding
- Other printed materials, printed papers or cardboard by folding, punching, embossing, gluing and laminating

In mechanical processes such as folding, binding and punching, no solvents are used. In processes such as gluing and laminating however, solvent-based products are generally used [85].

#### **B-9:** Incineration of Waste

The objective of waste incineration is to treat wastes so as to reduce their volume and hazard, while capturing (and thus concentrating) or destroying potentially harmful substances that are, or may be, released during incineration. Incineration processes can also provide a means to enable recovery of the energy, mineral and/or chemical content from waste [93].

Basically, waste incineration is the oxidation of the combustible materials contained in the waste. Waste is generally a highly heterogeneous material, consisting essentially of organic substances, minerals, metals and water. During incineration, flue-gases are created that will contain the majority of the available fuel energy as heat [93].

The organic fuel substances in the waste will burn when they have reached the necessary ignition temperature and come into contact with oxygen. The actual combustion process takes place in the gas phase in fractions of seconds and simultaneously releases energy where the calorific value of the waste and oxygen supply is sufficient, this can lead to a thermal chain reaction and self-supporting combustion, i.e. there is no need for the addition of other fuels [93].

The main stages of incineration process are:

- Drying and degassing here, volatile content is evolved (e.g. hydrocarbons and water) at temperatures generally between 100 and 300°C. The drying and degassing process do not require any oxidizing agent and are only dependent on the supplied heat
- Pyrolysis and gasification pyrolysis is the further decomposition of organic substances in the absence of an oxidizing agent at approx. 250 700°C. Gasification of the carbonaceous residues is the reaction of the residues with water vapor and CO2 at temperatures, typically between 500 and 1000°C, but can occur at temperatures up to 1600 °C. Thus, solid organic matter is transferred to the gaseous phase. In addition to the temperature, water, steam and oxygen support this reaction

 Oxidation - the combustible gases created in the previous stages are oxidized, depending on the selected incineration method, at flue-gas temperatures generally between 800 and 1450 °C [93].