RECYCLING OF NON-FERROUS METALS

Learning text

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Ostrava 2016
STUDY REGULATIONS

Recycling of Non-Ferrous Metals

For the subject “Non-ferrous Metal Recycling” in the 3rd semester of the follow-up studies of the branch “Progressive Technical Materials” you have obtained an educational lecture notes for the combined study comprising also study regulations.

1. Prerequisites

The subject has no prerequisites.

2. The objectives of the subject and outputs from the education

The aim of the subject is to introduce students to the fundamentals of non-ferrous metals recycling, characteristics of selected types of metal-based waste and metalline waste, overview of selected recycling procedures and basics of legislation relating to the waste management. A part of the subject is oriented on the integrated prevention, explanation of basic terms of toxicology and ecotoxicology and the effect of selected metals on the environment and humans.

After studying the subject, a student should be able to:

Knowledge:
- Describe and characterize the selected types of metal scrap,
- Describe and characterize methods of treatment of metal and metalline wastes, mechanical processing and used separation technologies, possibilities of recycling of selected types of wastes and their following utilization as secondary raw materials,

Skills:
- Evaluate ecological and economic aspects of utilization and processing of metal and metalline wastes as secondary raw materials,
- Apply the theoretical knowledge for recycling technologies and metallurgical industry.

For whom the subject is intended

The subject falls within the follow-up study of the branch “Progressive Technical Materials” of the study program “Materials Engineering”, but it can also be studied by applicants from any other branch.

Recommended procedure for studying each chapter:

The lecture notes are divided to parts – chapters, which correspond to the logical dividing of the studied subject matter, but they are not of the same volume. The assumed time for
the study of the chapter may differ significantly, therefore large chapters are further divided to numbered subchapters and these correspond to the structure of the lecture notes described below.

First, go through each chapter carefully. Then check-up whether you’ve learned the basic terms of the chapter. If not, we recommend to go back to look for the given term in the text. Answer the questions to the topic. After having comprehended the chapter, you can go on. The individual chapters mostly do not continue in the content of the previous ones, so chapters may be studied in an order by your own choice. The given time for studying the text serves only as a general guide.

**A way to communicate with lecturers:**

Within this subject, these lecture notes will be provided and a topic for a seminar project will be given. Topics and requirements for elaboration of the seminar project will be given over to students within tuition, or may be sent by e-mail upon asking a teacher. The elaborated seminar project can be sent 1x via e-mail to the teacher to be checked. After incorporating the comments, the corrected version will be given to the teacher via e-mail as well as in the printed form. All questions will be replied by e-mail, through contacting the teacher by sending an e-mail. For the e-mail communication we recommend to use the University e-mail address and to state the message subject properly. In extraordinary cases, the teacher may be also contacted by phone. Detailed instructions for studying and contacts to the teacher will be given to students at the beginning of the course in which they will be present.
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</table>
1. Introduction, basic terms, legislation

Study time: 2 hours

Objective
After reading this paragraph, you will be able to
- define the basic terms of waste management
- describe the basic distribution of waste and waste management activities

Lecture

All manufacturing and non-manufacturing activities are accompanied by the generation of waste.

- Waste
The term WASTE according to Act no. 185/2001 of the Coll. - **Waste is any movable item the owner disposes of or intends to or is obliged to dispose of.**

1.1 Distribution of waste

The division of wastes (basic, for normal use) depends on the terms of assessment, and the criteria can include, e.g. the origins, the properties of waste, its impact on the environment and on humans, etc.

Wastes can be divided:
- a) according to their basic physical characteristics:
  - solid
  - liquid
  - gaseous
  - mixed
- b) according to their origin:
  - industrial
  - construction
  - agricultural
  - municipal
  - overburden from surface mining
  - sludge from wastewater treatment plants
  - and others
- c) according to their environmental impact:
  - other
  - special - special waste, which is a harmful substance or which has significantly hazardous properties to humans or the environment (Fig. 1.1), it can also be hazardous waste.
Sources and occurrence of wastes

According to the source and the occurrence of wastes, they are divided into:

- circulation waste (production – own production, different production)
- new production waste (processing)
- amortization waste (consumer).

1.2 Waste management

Waste management is a set of actions aimed at preventing the generation of wastes, at waste treatment and the follow-up care of the sites where the wastes are permanently deposited, and the control of these activities.

The issue of waste management is primarily governed by Act no. 185/2001 of the Coll. - "Waste Act".

In compliance with the European Community law, this Act stipulates:

- rules for waste prevention and for waste management in compliance with the protection of the environment, the protection of human health and sustainable development,
- the rights and obligations of persons involved in waste management,
- and the competence of public administration authorities.

Waste management, according to the law, means in particular gathering, concentration, collection, purchase, sorting, shipping and transport, storage, treatment, use and disposal of waste.

The basic activities in waste management are:

1. Prevention of the occurrence of waste;
2. Reduction of the occurrence of waste;
3. Waste management:
   - Waste collection;
   - Shipments of waste;
   - Storage of waste;
   - Waste treatment;
   - Use of wastes;
   - Disposal of wastes.

The individual activities may overlap, complement and influence each other (Fig. 1.2).
The waste management is based on the prevention and reduction of the production of wastes. If the wastes already exist, they must be treated in such a way to maximize their use as secondary raw materials and to minimize their negative impact on the environment. Waste prevention is represented by waste-free or low waste technologies. These processes are, however, very energy intensive and the generation of waste is transferred into power supply.

## Waste management legislation

**Waste Act** - "Act no. 185/2001, on wastes and on the amendments of certain other acts", in short "Waste Act". This Act establishes an obligation to the originators and entitled persons to classify waste according to the Catalogue of Wastes for the purpose of waste management. Act stipulates, in compliance with the European Community law:

- rules on waste prevention and waste management while respecting the protection of the environment, the protection of human health and sustainable development, while reducing the negative impacts of the use of natural resources and the improvement of the efficiency of such use,
- the rights and duties of the persons involved in waste management,
- and the responsibilities of public administration authorities in waste management.

**The Catalogue of Wastes**

Decree no. 93/2016 of the Ministry of Environment, lays down the Catalogue of Wastes, the List of Hazardous Wastes and the lists of wastes and countries for the purpose of export, import and transit and the procedure for granting consent to export, import and transit wastes (the Catalogue of Wastes). The actual Catalogue of Wastes is presented in Annex of this Decree.

Wastes are classified under six-catalogue numbers of waste types, divided into three pairs of numbers. The first two digits refer to the group of wastes, the second two digits indicate the subgroup and the third two digits the type of waste.
Hazardous wastes in the list are marked with an asterisk (*) behind the catalogue number. Wastes without stars are classified as "other", i.e., they are not hazardous.
The waste catalogue contains 20 group of wastes.

Eg. 15 01 Containers
15 01 10* Containers with residues of hazardous substances or contaminated by these substances

List of hazardous waste properties is given in Annex no. 1.

- **Recycling**

Recycling = recirculation - returning back into the production process.
Waste recycling means the reuse of production, processing and consumption waste materials, substances and energies as a source of secondary raw materials in its original or modified form.
It can be considered as a strategy focused on reusing waste in order to preserve the natural resources and energies, while simultaneously reducing the impact of pollutants on the environment.
Recycling enables you to secure part of the raw material inventories, to reduce the production costs of raw materials and to reduce the environmental burden caused by production of waste.

- **Recycling technology**

Recycling is performed by means of a recycling technology. Recycling technology is a set of interconnected manufacturing processes, procedures and operations aimed at the conversion of waste into a secondary raw material.
Recycling technologies try to reduce the generation of waste by using low-waste technological processes, where the same manufacturing process or directly related processes use almost all the generated waste materials.

Low-waste technology is sometimes referred to as "waste-free technology".
It's such a method of production in which the most rational and most comprehensively utilize raw materials and energy in the cycle:
raw material sources - production - consumption - secondary raw materials.
Low-waste technologies are usually economically and energetically more demanding.

Conventional recycling technology – is recycling in terms of the treatment and reuse of already generated waste. The recycling technology in this case is a set of successive processes, procedures, technological operations, etc., aimed at the conversion of waste into a secondary raw material
A typical feature of recycling technology is its relative independence in the technological scheme:
production - waste - production.

While in case of low-waste technologies, the appropriate procedures for waste processing must be part of the production technology, the conventional recycling technologies are generally conducted separately - often in the form of additional investments designed to improve the economic and environmental efficiency of existing production processes.

- **Material flows**

It is very important to know the material flows. There are many illustrations of material flows - from the simplest ones, showing only the movement of materials (Fig. 1.3) - up to the balanced ones, showing the movement of material in the company.

Description of the picture:
- It introduces a material flow illustrating both the input of primary raw materials and the movement of secondary raw materials.
Reverse recycling requires a maximum reduction of $V_8$ output, both by minimizing the proportion of waste to be disposed of with no use, and by reducing the share of uncaptured losses by improving the technologies used to capture solid, liquid and gaseous products.

![Diagram of material flows](image)

Fig. 1.3 Scheme of material flows

- **Recovery of waste**

  Everyone is, during his/her activities or within the scope of his/her duties within the limits of the "Waste Act", obliged to ensure the priority use of wastes before their disposal. The material use of wastes takes precedence over other uses of waste.

  The possible ways of utilization of waste:
  - recycling of waste (organic waste composting, recycling plastic, glass, paper, metals, etc.);
  - energy utilization of waste (incineration);
  - recycling with energy use (biogas production from organic waste).


- **Methods of waste disposal**


- **Other basic terms**

  Other basic terms are set by Act 185/2001 of the Coll.

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<thead>
<tr>
<th><strong>Sumary of terms</strong></th>
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<tbody>
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<tr>
<td>Waste</td>
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<td>Waste management</td>
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</tbody>
</table>
Recycling
Recycling technologies
Material flows

Question to the topic

1. What is the definition of waste?
2. What are the types of waste?
3. What is the subject of the Waste Act?
4. What Catalog of waste contains and what it is used?
5. Explain the term of recycling, and what are recycling technology?

References

2. Waste processing

Study time: 2 hours

Objective  After reading this paragraph, you will be able to
- define the basic entering operations when
- describe the basic processes of waste processing

Lecture

Waste processing means the individual activities where a number of devices are used to crush, cut, and separate waste which is subsequently pressed, compressed, turned into packets, granulated, briquetted and packaged. The activities include manual or mechanical sorting and pre-sorting, etc.

The basic operations during the entry of waste into the treatment process typically include the size treatment of waste and the subsequent separation of the individual components of waste.

2.1 Desintegration

The size reduction of waste is a process which reduces the size of the input raw material items. The process includes crushing, grinding, cutting, shearing, hot-cutting, etc.

Crushing

Crushers are classified according to their construction and the method of disintegration. Types of crushers:
- Jaw crushers - grind material between a fixed and movable jaw (Fig. 2.1)
- Conical crusher - continuously grind the material between two concentric cones
- Roller crushers - the material is disintegrated between two counter-rotating rollers
- Swing hammer crushers - process the material by blows of hammers or bars (Fig. 2.1).


Fig. 2.1 Jaw crusher, hammer crusher
Waste processing

- **Grinding**

  Types of mills:
  - **Edge mills** - continuously grind the material and spread it by turning heavy wheels on a solid round plate
  - **Ball and rod mills** - the material is crushed by freely falling milling balls or rods Fig. 2.2.

- **Shearing**

  Scrap shearing is a very efficient process used for a variety of waste materials. Shearing uses a variety of shears:
  - high-performance hydraulic shears – the scrap is compressed in several directions prior to shearing, high performance equipment (Fig. 2.3)
  - mechanical shears - simple design, low acquisition and operating costs, a mobile version is very practical, used only sparsely, mostly for cutting wires and cables
  - alligator shears – the movement of the knife is ensured by an oscillating mechanism.

- **Cutting**

  Cutting can be performed by means of electric arc, plasma, laser or water jet. Hot cutting by flame is still very important.
Waste processing

- **Hot-cutting**

Hot-cutting by flame is used in cases where it is not possible to use a more economical method. The hot-cutting principle is based on using a mixture of flammable gases and oxygen heating the metal at the cutting point during combustion, so the particles burn and create a saw kerf.

- **Hammering**

Hammering is effectively used for size reduction of cast iron or for waste of brittle steels containing over 0.7% of C. Hammering takes advantage of the so-called cast iron hammers where cast iron scrap is hammered by lowering a hammer onto an impact zone where the cast iron is placed.

- **Rail breaker**

The method of size reduction is very specific and is used for cutting hard rods and profiles, but especially rails. A rail is inserted into the rail breaker by means of a roller conveyer. The rail is fixed by a roller; another roller equipped with a cutting knife is used to punch a shallow dent on the rail surface. The impact of the next and biggest roller breaks the rail at the point of the dent. This method is used to divide rails into pieces of the desired size (Fig. 2.4).

- **Cryogenic crushing**

Cryogenic crushing belongs to the special ways of the size reduction of wastes. During this process, the material is cooled to -100 up to -170 °C and then crushed. It uses the effect of material brittleness, which makes the crushing process easier. Cryogenic crushing is used for steel, rubber and plastics, which become brittle when cooled and lose their plasticity. On the other hand, this process is not used for most non-ferrous metals and their alloys and a significant part of non-metallic materials, because they retain substantial plasticity at low temperatures. The cooling medium is mainly liquid nitrogen.

- **Shredding**

For shredding (granulation) is used shredder (granulator). A metal scrap shredder, is a machine used for reducing the size of scrap metal. It is used for many types waste processing, e.g. wires and cables.
2.2 Compacting

Very soft wastes and wastes of small dimensions are compacted into larger pieces. This includes the processes of baling, briquetting, pelletizing and agglomeration.

☑ Baling process

The essence of baling is pressing scrap in hydraulic baling presses (Fig. 2.5). The scrap is pressed into so-called bales.

Fig. 2.5 Hydraulic baling press

☑ Briquetting

Briquetting is pressing waste by high pressures into the so-called briquettes (Fig. 2.6).

Fig. 2.6 High pressure briquette machine

☑ Pelletizing

Pelletizing or conglomerating is the basic method of compacting of fine-grained materials into pieces. The grains are palletized due to the rotational movement of the pelletizer, while moistening the material with water. The main reason behind good palletizing is the effect of capillary forces. Principle of pelletizing and pellets are given on the Figure 2.7.

☑ Agglomeration

Agglomeration or sintering is a thermal and chemical process of compacting of fine-grained materials. The batch is heated to a temperature at which the surface of grains melts, the individual grains are connected and caked forming sinter, the so-called agglomerate.
Waste processing

Fig. 2.7 Pelletizing, pellets

∑ Sumary of terms

At the end of the chapter are repeated the main terms that you should acquire:

Desintegration
Compacting

❓ Question to the topic

1. What are the methods of waste processing?
2. What are the methods of desintegration?
3. What are the methods of compacting?

References

3. Waste sorting

Study time: 2 hours

Objective

After reading this paragraph, you will be able to

- define the basic terms of metal waste sorting
- describe the basic processes of waste sorting
- describe selected sorting equipment

Lecture

The basic operations at the entry of waste into the process of its processing typically include the size waste treatment and subsequent separation of the individual useful waste components by means of technological processes based on different physical or physical and chemical properties of the waste components. Sorting is an integral part of these technologies.

3.1 The basic terms for metal scrap sorting

The basic terms for metal and metal-bearing waste containing non-ferrous metals are determined by the ČSN 421331 standard of "Wastes of non-ferrous metals and their alloys". This standard provides the following terminology:

- new waste - resulting from the production and further processing of non-ferrous metals and their alloys
- old waste - scrapped products and their parts, non-industrial collecting, etc.
- refining waste - unsorted wastes, mixtures and waste of inseparable metals and alloys that cannot be processed in any other way than by using the refining method. This group also includes non-ferrous metal waste with a higher than acceptable share of impurities, including mechanically admixed iron
- residues - waste containing non-ferrous metals in slag, dross, chemical compounds, sludge, etc.
- mechanical impurities - mechanically admixed metallic and non-metallic impurities
- sorting of waste according to material mark - sorting by the chemical composition determined by the applicable standard
- waste sorting by material classes - a common sorting of several material marks whose similar chemical composition allows processing together
- types of wastes - division according to shape, size, treatment, etc. respectively other properties (e.g. old waste, new, single-piece, formed, cast, pressed, cut, briquetted etc.).

New wastes and chips can be sorted according to their marks, while old wastes are sorted according to classes. Refining wastes are an exception. Coated or otherwise surface-treated wastes (varnished, enamelled, painted) are classified into the appropriate classes. They can be classified into types, the condition is, however, that the material with surface treatment does not interfere with the chemical composition and therefore the original quality (purity) of the waste. Wastes from two or more mixed metals are classified according to the prevailing metal.
Waste sorting

Waste classes

The individual classes of basic non-ferrous metal wastes and their alloys are described in detailed form in the following chapters.

Waste classes according to their markings:

<table>
<thead>
<tr>
<th>Class</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>3XX</td>
<td>Copper scrap and its alloys (eg. 321 Cu-Sn4 casting alloys)</td>
</tr>
<tr>
<td>4XX</td>
<td>Zinc scrap and its alloys (eg. 423 Zn min. 90% from galvanizing bath)</td>
</tr>
<tr>
<td>5XX</td>
<td>Lead scrap and its alloys (eg. 521 Pb-Sb alloy)</td>
</tr>
<tr>
<td>6XX</td>
<td>Tin scrap and its alloys (eg. 622 Sn bearing metals)</td>
</tr>
<tr>
<td>7XX</td>
<td>Nickel scrap and its alloys (eg. 721 Ni waste anode from electroplating baths)</td>
</tr>
<tr>
<td>8XX</td>
<td>Aluminium scrap and its alloys (eg. 812 Al-Cu-Mg alloys)</td>
</tr>
</tbody>
</table>

Class 9 includes wastes based on Ti, Mo, W, Co, Hg, Ta. The most important of these wastes are the wastes of tungsten and its alloys.

3.2 Metal scrap sorting

Waste metal sorting is based on the division of waste into components with the same or similar chemical composition corresponding to the given class of waste. The basic (casual) sorting of a waste material is carried out on the basis of the characteristic processing method (characteristic shapes - metals processed by forming, casting and other mechanical treatment methods) and the characteristic properties of metals, which include:

- **waste colour** - most of the materials have a gray-silver colour, only copper and alloys containing copper can have yellow and red colours.
- **magnetic properties** - apart from iron, we can also determine materials based on nickel. Magnetic properties are identified by a permanent magnet.
- **hardness** - soft materials include lead, aluminium; the hardness of brass also differs from aluminium bronze, etc. Hardness is determined by a scratch.
- **electrical properties** - electroconductive materials, non-conducting materials.

The sorting of metal wastes is carried out by various methods, from the very simple ones, when sorting is performed directly from heaps using sorting tables, up to the sorting lines, which are more efficient (Fig. 3.1). The sorting lines are equipped with material movement onto a sorting belt. These lines can be equipped either with upper or lower material hoppers. The sorting lines are equipped with other types separators - magnetic, eddy-current separator, ...).

![Fig. 3.1 Metal sorting line](http://jainhydraulics.com/shredder-metal-scrap-technical.html)
Waste sorting

- **Separation based on different magnetic properties**

Materials based on iron and non-ferrous metals make up a significant share of separated wastes, which is why they are given a lot of attention during waste processing. Ferromagnetic metals are the easiest to separate in a magnetic field using a permanent magnet or an electromagnet. The ferromagnetic material passing through is captured and separated from the remaining materials. The captured material is then carried away by a conveyor belt (Fig. 3.2). The magnet can be placed in a transverse (Fig. 3.3) or longitudinal direction (Fig. 3.4). In a transverse position, it can be placed virtually anywhere above the belt. In the case of longitudinal installation, it is necessary to place it at the cylinder head in order to use the parabolic material flow.

![Magnetic separation equipment](http://regulator-cetrisa.com/en/separation-equipment/)

**Fig. 3.2 Magnetic separation equipment from company REGULATOR-CETRISA**

![Magnet in a transverse direction](http://regulator-cetrisa.com/en/separation-equipment/)

**Fig. 3.3 Magnet in a transverse direction**
Waste sorting

Fig. 3.4 Magnet in a longitudinal direction

- **Separation based on different electrical properties**

Metals of high purity used as electroconductive metals (Al, Cu, ...), may be sorted on the basis of different electrical properties. These properties are determined by a device measuring the electrical conductivity value. The values of electrical conductivity for various materials are presented in Table 3.1.

<table>
<thead>
<tr>
<th>Material</th>
<th>Conductivity [MS/m]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silver</td>
<td>62.8</td>
</tr>
<tr>
<td>Copper</td>
<td>58.0</td>
</tr>
<tr>
<td>Gold</td>
<td>42.6</td>
</tr>
<tr>
<td>Aluminium</td>
<td>35.4</td>
</tr>
<tr>
<td>Aluminium alloys</td>
<td>17-34</td>
</tr>
<tr>
<td>Brasses</td>
<td>10-18</td>
</tr>
<tr>
<td>Bronzes</td>
<td>4-12</td>
</tr>
<tr>
<td>Chromium</td>
<td>6.7</td>
</tr>
<tr>
<td>Nickel-silver</td>
<td>4-5</td>
</tr>
<tr>
<td>Constantan</td>
<td>2.0</td>
</tr>
<tr>
<td>Titanium</td>
<td>2.1</td>
</tr>
<tr>
<td>Titanium alloys</td>
<td>0.5-2</td>
</tr>
<tr>
<td>Electroconductive Al</td>
<td>35.4 and high</td>
</tr>
<tr>
<td>Al 99.5</td>
<td>more than 34.0</td>
</tr>
<tr>
<td>AlMgSi</td>
<td>29-31</td>
</tr>
<tr>
<td>AlMg2</td>
<td>25-27</td>
</tr>
<tr>
<td>AlMg3</td>
<td>20-22</td>
</tr>
<tr>
<td>AlMg5</td>
<td>18-20</td>
</tr>
<tr>
<td>Dural</td>
<td>under 18</td>
</tr>
<tr>
<td>Al bronze</td>
<td>4-6</td>
</tr>
<tr>
<td>Red bronze</td>
<td>7-9</td>
</tr>
<tr>
<td>Brass 58</td>
<td>14</td>
</tr>
<tr>
<td>Brass 63</td>
<td>16</td>
</tr>
</tbody>
</table>
Waste sorting

The value of electrical conductivity can be measured, e.g. by means of a Sigmatest device (Fig. 3.5). The electrical conductivity is determined by the method of eddy currents, and it is necessary to know the exact values of the electrical conductivity of the material in question (Tab. 3.1).

Fig. 3.5 Device SIGMATEST 2.069

- **Determination of chemical composition**

An exact analysis of the chemical composition of metal wastes takes advantage of various analyzers. The most commonly used ones are optical emission spectrometers and X-ray spectrometers. Both types of devices can be of stationary and mobile version.

**Optical emission spectrometers**

The most commonly used types are optical emission spectrometers with spark excitation, where the source unit generates high voltage sparks between the prepared sample and the counter electrode in a controlled argon atmosphere. Spark discharge is used to vaporize material from the sample surface inside the discharger, and atoms and ions, which emit light of their characteristic wavelength, are excited during this process (Fig. 3.6, 3.7).

Fig. 3.6 CCD optical system
Waste sorting

Fig. 3.7 Optical emission spectrometer SPECTROMAXx - stationary

X-ray-fluorescent spectrometers
X-ray, respectively X-ray-fluorescent spectrometers are analyzers where the excitation of a characteristic radiation is carried out by means of an X-ray tube or a radioisotope (Fig. 3.8). Handheld X-ray spectrometers are ideal for waste sorting (Fig. 3.9, 3.10).

Fig. 3.8 The principle of measuring X-ray fluorescence analyzer

Fig. 3.9 X-ray spectrometer SPECTRO xSORT
Eddy-current separation

For separating non-magnetic metals can be used non-ferrous metal separator, which works on the eddy currents. Sorting is based on the principle, that each conductive object that enters into the variable magnetic field, is magnetized. Magnetic separator system includes a high performance magnetic roller of NdFeB magnets rotating at high speed. Conductive particles are discarded of sorted material (Fig. 3.11).

Fig. 3.11 Eddy-current metal separator

Sumary of terms

At the end of the chapter are repeated the main terms that you should acquire:

Waste classes, sorting options
Waste sorting

Separation based on different magnetic properties
Separation based on different electrical properties
Determination of chemical composition

Question to the topic

1. How to marking waste classes of metal waste?
2. How to sort scrap metal?
3. What equipments are used for separation?
4. What equipments are used for determination of chemical composition?

References

4. Waste of copper and copper alloys

Study time: 3 hours

Objective
After reading this paragraph, you will be able to
- define waste copper and its alloys
- describe pyrometallurgical methods of copper scrap processing
- describe hydrometallurgical methods of copper scrap processing

Lecture

4.1 Copper and its alloys

Copper is reddish metal, which excellently conducts electricity and heat - very high thermal and electrical conductivity. It is a malleable and ductile metal, corrosion-resistant, because the formed oxide layer protects it from further corrosion. According to the technical classification of metals include copper to the group of general (heavy) non-ferrous metals with medium melting point.

Properties:
- Symbol: Cu (Cuprum)
- Atomic weight: 63.54 g·mol⁻¹
- Density: 8.94 g·cm⁻³
- Melting point: 1083 °C
- Boiling point: 2595 °C

Application:
The use of copper is very wide and extends into many industrial fields, including engineering, foundry, chemical and electro-technical industry, as well as glass and textile industries. Copper is mainly used in the production of electrical wires and alloys. It is also used in surface treatment.

The most frequently used copper alloys are brass and bronze. Brass, Cu and Zn alloys are divided according to the zinc content into brasses and tombacs.

4.2 Characteristics of copper and copper alloy wastes

Copper waste can be divided into various types according to various criteria. Part of the waste generated during the production of formed or cast semi-finished products is returned back in the furnace and again becomes a material component of the first melting. Part of the waste is re-melted immediately in the production plant and, after an analysis, it goes back into production as the material of the first or second melting. The production of second smelting alloys uses all the waste generated from discarded machines, devices and objects of daily consumption.

Copper consumption by sectors is as follows:
- Electrotechnical industry 54 %
- Building industry 15 %
- Machine engineering 13 %
- Transport 11 %
- Other 7 %
Wastes of copper and copper alloys

ČSN 421331 standard says that the wastes of copper and copper alloys can be divided into:

- Pure waste without the presence of any impurities
- Refining waste, i.e. waste mixed with other metals (polymetallic wastes)
- Residues, i.e. waste in which there is metal in the form of any compound (dross, ashes, galvanic sludge etc.).

According to this standard, waste is divided according to its place of presence into production, processing and consumer waste:

- Production waste is waste of metallurgical and foundry productions. This waste includes bosses, gates, casting scrap, cuttings, splinters and scrap from rolling, forging and pressing (i.e. new waste). This waste can be safely put into melting furnaces, even without checking the chemical composition.
- Processing waste is produced during the processing of semi-finished products in engineering plants, workshops etc. It includes chips, cuttings, segments, scraps from pressing, machining etc. This waste is also referred to as new waste.
- Consumer waste represents sorted and removed parts and components from maintenance or from discarded machines and equipment, worn off or unusable objects, e.g. scrap wires and cables, collected metal waste, etc. This waste is referred to as old waste.

Pure copper and copper alloy wastes include:

- electroconductive copper - especially cables and wires (waste containing 99.8 % of Cu)
- pure copper - for structural purposes (Cu content of 99.5 %)
- tin bronze – Cu-Sn tin content of 0.8-13 %,
- aluminium bronze – Cu-Al aluminium content of 5-10 %, can also contain Fe, Ni. Fittings, bearings, machine parts,
- nickel bronze – Cu-Ni (Ni 30-45%), nickelin, capacitors, for shipbuilding, constantan, electrical engineering,
- lead bronze – Cu-Pb content of Pb of 20-30 %,
- red bronze – Cu-Sn-Zn (Sn 5-10%, Zn, Fe, Cu res.) fittings, pumps, pans, valves, etc..
- Ms 95 – tombac
- Ms 90 – red tombac
- Ms 85 – “gold” tombac
- Ms 80 – white tombac
- Ms 70 – yellow tombak
- Ms 67,68 – “semi-tombac”
- Ms 58-63 – brass
- Ms 60Sn – sound brass
- Ms45Ni14 – nickel brass.

These pure materials are molten as secondary materials after their sorting and precise specification, and the melt is used in foundry industry after fine alloying. The melting processes and the processes of further refining of these waste materials adhere to the following methods.

### 4.3 Sorting of copper waste

This waste is sorted according to its chemical composition, according to the shape and dimensions, respectively according to the degree of contamination with mechanical impurities (depending on the types). The most important classification is by chemical composition, which is made essentially in two ways, either by marks material, or by class. When sorting the use optical emission or X-ray spectrometers.

Only new waste is sorted according to material marks if present in larger quantities. Smaller amount of waste or old waste is sorted according to classes, which are indicated according to the base metal content and the processing.
Waste is divided into nine groups according to its shape:
1. new lump waste,
2. new sheet metal waste,
3. new waste of uninsulated wires,
4. old lump waste,
5. old sheet metal waste,
6. old waste of uninsulated wires,
7. waste of insulated wires and cables,
8. chips,
9. residual material.

Each group has several sub-groups according to dimensions, e.g. according to another characteristic property (e.g. new lump untreated waste, suitable for smelting in a furnace, suitable for smelting in crucibles, etc.).

Waste treatment is the first part of the work procedure during the processing of waste.

Fig. 4.1 Cu pipe waste – purity 99.5 % Cu
Fig. 4.2 Pure Cu lacquered wire
Fig. 4.3 Cu wire with Cd
Fig. 4.4 Cartridge cases – brass BS70
Fig. 4.5 Cu braided wires
Fig. 4.6 Tinned copper scrap
Waste treatment involves the removal of adulterants and impurities that are contained in it, either freely or they are firmly bound together – mixed waste is sorted into the individual groups and types. After that, it is adjusted to the shapes and dimensions suitable for putting in furnaces and other metallurgical equipment. Dimension adjustment means the procedures described in the previous chapters. Figures 4.1 to 4.6 present some of the pure wastes of copper and copper alloys.

### 4.4 Processing of copper and copper alloy scrap

The sorted wastes are mostly processed using a pyrometallurgical method – they are melted in smaller melting furnaces using different types of heating or they can be melted directly in a shaft furnace. Some types of wastes can also be processed by means of hydrometallurgical and electrometallurgical method.

#### 4.4.1 Pyrometallurgical processing of copper scrap

- **Scrap copper, brass and bronze melting**

Waste copper, brass and bronze melting is carried out in smaller melting furnaces with different types of heating systems provided that the material is sorted according to mark or a group of similar marks. This is a relatively pure material, which does not have to be melted with refining waste or the residues. This melted and refined material is further industrially processed.

1. **Melting copper scrap, brass and bronze in smaller melting furnaces**

A number of melting devices are used for the melting processes. They include stationary, rotary, hearth, and electric arc furnaces, induction furnaces of channel or crucible type, gas furnaces and others. To accelerate the melting of a large volume of pure metal, you can use shaft furnaces.

Dosing is the basis of good melting process. First, you have to dose lightweight waste (sheets, wires) processed into bundles by pressing, followed by lump waste. This way the material is put in a heated furnace at the temperature of 1350 - 1450 °C. Covering salts are added to the molten metal.

The cover layer prevents the reaction of the melt with the furnace atmosphere, ensures the gasification, i.e. the absorption of the individual components of the atmosphere into the metal, and it reduces the intensity of volatilization of the volatile components of Sn and Zn.

Covering salt and additives used to ensure melt refining are added into electric resistance furnaces in case of copper and copper alloys. The refining additives include Cu dross, SiO₂ sand or sodium nitrate NaNO₃.

Bronze materials are mostly melted in hearth furnaces or in crucible furnaces. The protective layer is charcoal, cryolite, fluorite, and soda ash.

The melting of brass mostly takes advantage of electric induction furnaces of a channel type. Coke is used as the covering layer (Fig.4.7).

![Fig. 4.7 Melting of brass in electric induction furnace](image-url)
2. The refining processes of copper, brass and bronze

The purpose of the refining process is to reduce the content of gases (hydrogen, oxygen), and to remove non-metallic inclusions and impurities.

a) The removal of dissolved metal impurities of Fe, Al, Si, Mn

The removal of these metals is carried out so by the so-called oxidative refining, where the melt is bubbled with air, steam or where copper dross is added to the melt. The basic reactions of this process are:

\[ \text{Cu}_2\text{O} + \text{Me} = 2 \text{Cu} + \text{MeO} \]
\[ 2 \text{Cu}_2\text{O} + \text{Cu}_2\text{S} = 6 \text{Cu} + \text{SO}_2 \]

The process takes place at the temperature of 1100 - 1160 °C, and it is used in particular for bronzes containing less than 3% of Sn. The removal of the present Cu\textsubscript{2}O dissolved in Cu is carried out using a deoxidising agent P (most common), Li, B, Ca:

\[ 5 \text{Cu}_2\text{O} + 2 \text{P} = \text{P}_2\text{O}_5 + 10 \text{Cu} \]

Combined deoxidising, first using P and then Li, is performed as well.

b) The removal of dissolved gases in the alloy (hydrogen)

Hydrogen getting into melt from the moisture of the charge. Another source of hydrogen is methane CH\textsubscript{4}. Hydrogen must be removed from the melt, because it causing porosity in the castings. The reduction of the content of hydrogen is carried out using inert gases Ar, N.

3. The removal of insoluble oxide inclusions

The removal of insoluble oxide residues is carried out by active filtration (trapping inclusions on a filter as a result of adsorption or chemical sorption) or inactive filtration (mechanical retention of impurities).

4. Melting copper scrap and copper alloys in a shaft furnace

Waste copper and copper alloys are often melted in a shaft furnace. These furnaces are used to process less valuable copper wastes, such as small electric motors, copper-plated sheet metal, slag, pellets, amortization waste, electrical waste etc. (Fig. 4.8). Lower-quality types of fine-grained unsorted wastes must be compacted (pelletisation or agglomeration). This conventional pyrometallurgical recycling comprises of the following stages (Fig. 4.9):

4. 1. Melting in a shaft furnace
4. 2. Converter process of black copper
4. 3. Pyrometallurgical refining
4. 4. Electrolytic refining.

Fig. 4.8 The charge into shaft furnace
Melting in a shaft furnace is a reducing process, where the charge consists of: lump waste, agglomerate, coke, limestone, dolomitic limestone, and silica. The product is the so-called black copper (80-87% Cu), which is further processed.

The converter process of black copper is carried out in a copper converter (Fig. 4.9, 4.10). The converter process removes impurities. Reducing the impurity content of Pb, Zn, Sn, Fe, Sb, As is ensured by oxidizing melting. The converter process product is rough copper (97-98.5% Cu) intended for pyrometallurgical refining.

Pyrometallurgical refining of Cu is melting of rough copper in flame furnaces with acidic lining. The impurities are oxidised by air blown into the metal bath and the impurities pass into slag. The result of this pyrometallurgical refining is metallurgical copper with the Cu purity of 99.5 to 99.8%. Metallurgical anode copper is cast into anodes and then it is electrolytically refined (Fig. 4.12).
Electrolytic refining

The electrolytic refining of copper is a process during which the action of direct electrical currents leads to a gradual dissolution of copper anode and the subsequent separation of copper on the cathode. This process is shown schematically in Figure 4.13.

![Scheme of electrolytic refining of copper](http://www.funscience.in/study-zone/Chemistry/Metals/PurificationOrRefiningOfImpureMetals.php)

The electrolyte is a solution of copper sulphate acidified with sulphuric acid. The impurities are collected in the so-called anode mud (mainly precious metals) and are partly dissolved in the electrolyte. The process temperature is maintained between 50-60 °C. The entire process, which is called refining electrolysis, can be illustrated as follows:

Cu cathode – high purity plate / solution CuSO₄, H₂SO₄ / Cu anode

Processes at the anode ..... \( \text{Cu} = \text{Cu}^{2+} + 2e^- \)
Processes at the cathode ..... \( \text{Cu}^{2+} + 2e^- = \text{Cu} \)

The product is cathode copper with the min. purity of 3N8. Anode mud is a valuable source of precious metals.
A general overview of pyrometallurgical processing of metal waste based on copper and copper alloys in a shaft furnace is shown in Fig. 4.14.
4.4.2 Hydrometallurgical processing of copper scrap

Hydro-metallurgical processing of copper is carried out on a smaller scale than pyrometallurgical processing. It mostly deals with the processing of polymetallic wastes or products acquired from other processes. Hydro-metallurgical processes consist of pre-treatment processes, materials for further hydrometallurgical processing, and the actual hydrometallurgical processes.

- **Pre-treatment of wastes**

This procedure must be performed if the surface of waste is contaminated by greases, oils, or paints, which would prevent the flow of agent to the metal surface. The removal of these impurities can be carried out by burning (combustion of impurities) or by degreasing in hot solutions of sodium carbonate \( \text{Na}_2\text{CO}_3 \) with added sodium hydroxide.

- **Hydrometallurgical processing**

It is based on chemical processes - the action of aqueous solutions of chemical agents. The leaching process usually takes advantage of sulphuric acid, which can be used to process especially compact copper waste, copper dross or anode mud from copper electrolysis. The leaching process can take place under normal conditions in tanks under continuous stirring and aeration at a temperature of 75-85 °C, or these processes can take place in an autoclave at higher temperatures and pressures. The final stage of the process is the extraction electrolysis, which takes place in a system with an insoluble lead cathode \( \text{Pb}^{+}/\text{CuSO}_4/\text{Cu}^- \).

Ammoniacal leaching is another procedure which uses mixed leaching agent of ammonium carbonate with ammonia or ammonium sulphate with ammonia. The leachate is processed by means of ammonia-distillation condensation, where CuCO₃ precipitates from the \([\text{Cu(NH}_3]_4\text{CO}_3]/\text{complex} \). It does not create iron aminocomplex and it is easily separable from copper.

Several examples of hydrometallurgical procedures of copper processing can be presented from the procedures described above:
1. **Production of copper sulphate**

Production of copper sulphate is a procedure of waste copper processing (especially from anode mud), and the final product is not metallic copper, but a chemical compound – copper sulphate. Waste copper is leached in sulphuric acid with simultaneous mixing and aeration using oxygen. The reaction itself is as follows:

\[ \text{Cu} + \text{H}_2\text{SO}_4 + \text{O}_2 \rightarrow \text{CuSO}_4 + \text{H}_2\text{O} \]

Copper sulphate is subsequently produced by crystallization. The scheme is shown in Fig. 4.16.

![Scheme of copper sulphate production](image)

Fig. 4.16 Scheme of copper sulphate production

2. **Processing of waste electric motors**

The processing of waste electric motor is one of the methods using ammoniacal leaching of copper metal present as Cu wires in the waste. The overall processing procedure is as follows:

- removal of rotor from the stator
- annealing at 500-600 °C in order to remove paints, varnishes and greases
- leaching in ammoniacal solution of ammonium sulphate resulting in a formation of a complex \([\text{Cu(NH}_3]_4\text{SO}_4]/\)
- after the decomposition, the leach is further processed by extraction electrolysis using an insoluble Pb anode

\[ \text{Pb}^+ / [\text{Cu(NH}_3]_4\text{SO}_4 / \text{Cu}^- \]

3. **Separation of copper from weak solutions**

This separation is carried out in solutions having a low copper content, where the processing is performed:

- to metal - cementation using Fe
- to chemical concentrate – precipitation.
Wastes of copper and copper alloys

4. Other processes

The other processes involved mainly in the processing of weak leachates in order to increase the concentration of copper in the leach include the extraction and adsorption processes and the ion exchange process.

4.5 Toxicity of copper

Copper belongs among essential elements for the human organism. It is necessary for growth and development of bones, connective tissues, brain, heart and other organs. Cu is important for creation of hemoglobin and some enzymes and for iron absorption and metabolism. It is also important for effective utilization of vitamin C. Deficiency of copper in children results in the physical and mental retardation. High doses of copper cause stomach ache and intestinal pain, insult of livers and kidneys and anemia. Some copper compounds irritate skin, may cause inflammations after repeated exposures. They may also initiate conjunctivitis. Copper is an essential element for animals and higher plants, however, in higher amounts is considerably toxic for water organisms (algaeicides).

∑ Sumary of terms

At the end of the chapter are repeated the main terms that you should acquire:

Wastes of copper and its alloys
Processing of copper scrap and its alloys

❓ Question to the topic

1. What are the types of copper waste?
2. How are separated copper scraps?
3. What are the pyrometallurgical methods of copper scrap processing?
4. What are the hydrometallurgical methods of copper scrap processing?

📖 References

5. Lead wastes

Study time: 2 hours

Objective After reading this paragraph, you will be able to

- define lead and its alloys waste
- describe methods of lead waste processing
- describe the basic components of car batteries and how its recycling

Lecture

5.1 Lead and its alloys

Lead has a low thermal and electrical conductivity. It is resistant to concentrated acids and other chemical agents. It is a malleable and ductile metal. Lead has good castability. These properties give it great functional value, both in its pure form or in alloys and compounds. The vapours and compounds of lead are poisonous! According to the technical classification of metals include lead to the group of general (heavy) non-ferrous metals with low melting point.

Properties:

Symbol Pb (Plumbum)
Atomic weight 207.19 g·mol⁻¹
Density 11.34 g·cm⁻³
Melting point 327.4 °C
Boiling point 1744 °C

Application:

Lead has been used since ancient times, but its use has recently been restricted due to its proven toxicity. The critical operational temperature is 550 °C, because at this temperature the melt shows intensive volatilization of lead into the atmosphere. Its use, however, is in many cases necessary, it is most often used in the manufacturing of batteries, from which it is subsequently recycled. Another use of lead is as a protection against X-rays, and as an anti friction metal. It is also used for the production of underground cables (sheathing), ammunition, solders, tanks for sulphuric acid etc. Lead is a hazardous metal and waste containing lead is classified as hazardous waste.

The most frequently used lead alloy is the so-called antimonial lead containing 0.5-17% of antimony, thereby increasing the hardness and strength of the material. This alloy is used for grids of accumulators and equipment for the chemical industry. Other uses include leaded solders - Pb alloy with tin, with added cadmium, silver or copper. These alloys with low melting temperatures are used in electrical and radio engineering. Nowadays, their use is restricted and they are replaced by lead-free solders. The anti friction metals are the alloys of Pb-Sn-Sb with the addition of Cu and Ni.

5.2. Characteristics of lead wastes

According to standard, lead wastes can be divided into:

- Pure Pb - chippings during machining
- Antimonial lead - lead alloys with antimony (Sb to 10%)
Lead wastes

- Bearing metals - content Sn max. 10%, Sb max. 15%
- Soft Pb - cable sheathing (impurities of up to 5%)
- Pb residues - slag, ash, dross, flue dust
- Battery lead - either in the form of plates or as the whole batteries

Some types of the lead waste are on the Fig. 5.1-5.4.

![Fig. 5.1 Pb batteries without acid](image1)
![Fig. 5.2 Pb boards from the batteries](image2)
![Fig. 5.3 Pb batteries with acid](image3)
![Fig. 5.4 Pb soft wastes from cables](image4)

### 5.2.1 Lead batteries – the most common lead waste

A car battery (Fig. 5.5) consists of a container (plastic – polypropylene, previously also ebonite or PVC), plate electrodes (positive - PbO₂, negative - spongy lead), a separator (plate of electrically non-conductive material which is interposed between two electrodes), and an electrolyte (usually H₂SO₄ + H₂O, with density 1.285 kg/dm³).

The processing of waste lead batteries can be divided into:
1. Processing involving mechanical treatment
   a) Complete separation of batteries
   b) Partial separation of batteries
   c) Separation using cryogenic technique and subsequent hydrometallurgical processing.
The essence of the processing of waste batteries is the separation of the individual components of the batteries. The batteries are deprived of acid, crushed and sorted into different fractions using automated equipment (MA a CX processes). After the sorting process, there are components that can be used again, such as lead grilles, sulphate paste, sulphuric acid and polypropylene.

2. Direct metallurgical processing - VARTA technology is used in Kovohutě Příbram nástupnická, a.s.

3. Processing of battery residues.

Processing of spent lead acid batteries providing valuable secondary raw materials. Secondary lead is mainly used again for the production of new batteries (Fig. 5.6, 5.7).
5.3 Sorting and processing of lead wastes

Lead wastes are processed using pyrometallurgical method. Depending on the type of waste and its quantity, you can choose different types of furnace units:

a) Smelting in kettles
b) Smelting in hearth furnaces
c) Smelting in short drums furnaces
d) Smelting in electric furnaces
e) Smelting in shaft furnaces.

a) Smelting in kettles

Smelting in kettles is the easiest method of processing waste Pb due to the low melting point of 327.4 °C. Pb wastes processed in this way include coils, foils, waste from cables, from chemical equipment, tanks etc. The melting temperature is kept at 500-550 °C, because lead evaporates at higher temperatures. The melting takes place below a layer of wood coal, lead after melting is mixed and the temperature is lowered to 450 °C, the dross is removed and the lead is cast.
b) **Smelting in hearth furnaces**

The advantage of this method is that it allows you to process fine powder materials without their sintering beforehand. The hearth furnaces are used to process waste containing a higher amount of oxides, sulphides or sulphates. These wastes also include waste from lead batteries. The melting temperature is more than 900 °C. After dosing, the charge is heated to 900 °C - 1050 °C until the charge completely melts. The melt is then allowed to stand for a while in order to let the necessary reactions take place and to separate the slag. After that, the lead is discharged into a boiler and it is allowed to cool to approximately 390 °C. This is followed by a discharge of slag from the furnace, which is subsequently processed in shaft furnaces. The basic reactions during the melting in hearth furnaces:

\[
PbSO_4 + PbS \leftrightarrow 2Pb + 2 SO_2
\]

**c) Smelting in short drum furnaces**

The charge of short drum furnaces may include fine battery waste, fine ash, slag, as well as weak residues. A drum rotary furnace is shown in Fig. 5.8. The rotational speed of the furnace is 1-8 rev/min, and the melting temperature is 1100-1200 °C. The heat is supplied by gas burners, while the lining heats up and passes the heat onto the charged material. The disadvantage is the short life of the lining.

![Fig. 5.8 Short drum furnace](image)

d) **Smelting in electric furnaces**

Electric resistance furnace is used for smelting of secondary materials, where open melt bath covered with coke is used. The raw materials are fed to the surface of the bath, where they react and produce metal and a small amount of slag. The metal and slag are continuously and periodically discharged.

e) **Smelting of battery Pb waste in a shaft furnace**

The processing of lead and lead residues in a shaft furnace is the most common procedure how to process these types of wastes. Fine lead dust and residues must be briquetted or agglomerated prior to their use in order to avoid clogging of the charge column. The content of the fine fraction may be up to 25%. The processes taking place in a shaft furnace have a reduction character (reducing agent - carbon monoxide). We get crude lead, a lead grit and slag (Fig. 5.9, 5.10).
The charge fed into a shaft furnace during the processing of battery waste includes:
- batteries without acid, battery plates, soft lead, and during the so-called silver campaign, it could also be waste from photographic industry, electrical waste
- returnable slag
- lead matte
- coke
- limestone
- silica, respectively leaded glass (screens)
- Fe chips
- sodium carbonate.

**Refining crude lead**

Crude lead contains unwanted impurities, especially copper, zinc, tin, antimony, bismuth and precious metals that enter the charge during the processing stages of electric waste or waste from the photographic industry. Unwrought lead contains 95 to 96% of Pb, and refining increases its content to 99.5% (Fig. 5.11).

Individual stages of refining are as follows:
1. The removal of dross and copper is performed by simple mixing-off at temperatures around 500 °C. Mechanical impurities leave due to density difference on the surface of the lead bath, where are downloaded.
2. The removal of arsenic, tin and antimony from lead takes advantage of their greater affinity for oxygen in comparison with lead. There are two ways used for their oxidation on industrial scale nowadays: oxidation with oxygen and oxidation with sodium nitrate (Harris process).
3. The removal of precious metals from lead using Zn - precious metals, especially gold and silver are removed from lead using the Parkes process. This method is based on the ability of metals to create intermetallic compounds with metal zinc having a higher melting temperature and lower density than lead.

Fig. 5.11 Refining and casting of pure lead

5.4 Toxicity of lead

Lead has not an essential significance for humans. 90 % of accepted lead tends to accumulate in bones, negatively influencing haematogenesis, because it blocks production of hemoglobin. Lead ions are carcinogenic and lead is classified as a probable carcinogen for human lungs and kidneys. Typical symptoms of lead poisoning are paleness of face and lips, constipation and loss of appetite, colic, anemia, headaches, abdominal cramps, chronical kidney nephritis, brain damage and malfunctions of the central brain system.

Treatment consists in a procedure known as chelation therapy – binding to accumulated lead, which is then excreted in urine. Even traces of lead in surroundings and food may result in permanent supply into the organism and subsequent serious diseases, because lead accumulates in the body and can be excreted only with difficulties.

Lead is hard to get rid of for the body. As soon as lead enters the organism, it is deposited in bones and teeth. Lead may end up there for many years and gradually releases to blood, from where slowly excretes through kidneys to urine and through livers to bile.

∑ Sumary of terms

At the end of the chapter are repeated the main terms that you should acquire:

Wastes of lead and its alloys
Processing of lead wastes and its alloys
Car baterries recycling

❓ Question to the topic

1. What are the types of lead waste?
2. How are separated lead wastes?
3. What are the pyrometallurgical methods of lead waste processing?
4. What are the basic components of car batteries and how are recycled?
Lead wastes

References


6. Wastes of aluminium and aluminium alloys

Study time: 2 hours

Objective After reading this paragraph, you will be able to
- define aluminium and its alloys waste
- describe methods of aluminium waste processing

Lecture

6.1 Aluminium and aluminium alloys

Aluminium is metal with very high thermal and electrical conductivity. It is a malleable and ductile metal, corrosion-resistant, because the formed oxide layer protects it from further corrosion. According to the technical classification of metals include aluminium to the group of light non-ferrous metals with medium melting point. With other metals it creates many alloys which are widely used in the industry - alloys have low density and sufficient strength.

Properties:
Symbol       Al (Aluminium)
Atomic weight 26.98 g·mol⁻¹
Density       2.699 g·cm⁻³
Melting point 660.5 °C
Boiling point 2520 °C

Application
The application of aluminium is very wide and extends into many industrial fields, including engineering, foundry, steel industry as a deoxidizing agent, chemical and electrical industries, packaging technology, manufacture of glass, paints and pigments and water management.

Alloys:
- Al-Si – silumins - are intended for casting
- Al-Si-Mg, Al-Si-Cu, Al-Si-Cu-Ni, Al-Cu, Al-Mg – other alloys intended for casting
- alloys of Al-Cu-Mg, Al-Mg-Si, Al-Zn-Mg, Al-Zn-Mg-Cu type (hardenable) - are intended for forming
- alloys of Al-Mg, Al-Mn type (non-hardenable) - are intended for forming.

Application of alloys:
- engineering (castings, structural components, various profiles, etc.)
- automotive industry (engine parts, profiles for door panels, shock absorber housings, etc.)
- aerospace industry (use of alloys based on Al-Li)
- food industry (packaging technology – aluminium foil)
- electrical industry (cables, wires)
- building industry (facade profiles, profiles for doors and windows, etc.).

6.2 Characteristics of aluminium wastes

According to ČSN 421331 standard, waste aluminium and its alloys can be divided into:
A. Wrought aluminium
- Al formed with the min. purity of 99.5% suitable especially for electrical purposes, metallurgical,
- Al-Cu-Mg alloys (dural) with content Cu max. to 8%, Mg max. 1.9 % and Si, Mn, Fe
- Al-Mg (hydronal) alloy with Mg max. 7.0 %
- Al-Cu-Mg-Ni with content Cu max. 4.5%, Mg max. 1.8%, Ni max. 2.25%
- Al-Zn with content Zn max. 7.0%, Cu max. 2%, Mg max. 2.8%
- Al-Si (silumin) with content Si max. 13%, Cu max. 1.3%, Ni max. 1.3%
- other wrought alloys
B. Foundry aluminium
- Al-Si (silumin) Si max. 13%, Mg max. 0.4%, Mn max. 0.5%
- Al piston alloys Si max. 22%, Cu max. 2%, Ni max. 2%
- Al-Mg with content Mg max. 11%
- Al-Si-Cu with content Si max. 11%, Cu max. 8.5%
- aluminium residues and its alloys - dross, slag, ashes etc.
- unsorted waste aluminium and aluminium alloys.

Fig. 6.1 The common grades of aluminium scrap

The common grades of aluminium scrap:
- Mixed cast alloy
- Aluminium brass condenser tubes
- Clean lithographic sheets
- Mixed low copper aluminium clippings and solids
- Clean mixed old alloy sheet
- Can stock, new and old
- Aluminium copper radiators
Aluminium nodules
New warw and cable, pure or mixed
Old wire and cable
Pistons, borings, turnings and foil
Sweated aluminium
New aluminium ally clippings and solids, segregated or mixed
Segregated new aluminium castings, forgings and extrusions
Auto and airplane castings
Insulated wire and fragmented scrap from automobile shredders
Aluminium-lithium alloys…

6.3 Processing of aluminium wastes

From the viewpoint of lifetime, aluminum has a different period of application. Thin-walled containers have a very short lifetime (foils, beverage cans,…).
Aluminium wastes

Aluminium scrap may contain a range of impurities, which may make it difficult recycling (lacquers cans, insulation, oil, emulsion,…). In this case these can be removed via pretreatment processes or in the melting furnaces. The recycling process of waste is difficult for scrap such as used beverage cans and aluminium chips or turnings. Recycling of lump scraps is generally simpler. Processing of all aluminum scrap is possible and desirable (Fig. 6.2). When remelting Al scrap leads to significant energy savings and a lot of primary raw materials. The problem is the oxidation of aluminum. The big problem for environment is producing of slags, which are hazardous waste.

A suitable furnace is chosen according to the type of scrap, depending on the amount of impurities, by the volume of waste and by other parameters. Scrap processing can be simply described with the following steps:

- Aluminium scraps are sorting by chemical composition and by other parameters (lacquered/non-lacquered, lump/thin-walled scrap,...).
- The material is inserted into the furnace and smelted.
- The salt fluxes are added to cover the molten metal to remove impurities and meanwhile protect metal from oxidisation.
- Liquid metal is transferred to holding furnaces. This is performed refining (de-gassing, reduction of Mg (a process known as “de-magging”) and alloying.
- The melt is casting into ingot or slabs, ...

### Smelting of Al waste

The actual smelting of aluminium is largely influenced by the high capability of aluminium to react with gases (oxygen, hydrogen, nitrogen, water vapour, CO₂, hydrocarbons). This negative property of aluminium causes the formation of an oxide layer. Fluxing agents and covering salts (a mixture of NaCl and KCl with 3–5 % of Na₃AlF₆) are used as a protection against the effects of gases on the melt of aluminium. These compounds have the following objectives:

- protection against oxidation and gassing
- dissolution of the produced oxides.

The following furnaces are used for aluminium smelting:

- hearth - one, two or three -chamber ones with a forehearth
- shaft furnace
- rotary drum furnace
- induction furnaces of channel or crucible type.

### Processing of Al residues, dross, ashes

Al residues, ashes and dross represent a large volume of material acquired during the processing of waste aluminium. This material consists of oxides and metal. The use of refining salt results in the occurrence of aluminium chlorides, which belong to the group of hazardous wastes. They must be stored separately in covered areas. They decompose by the effect of moisture and they may get into ground water.

The processing of this type of waste is carried out:

- using the wet method
- using the dry method.

**A. The dry method – Aerofall mill**

The essence of this method is the grinding of waste in a short ball mill without the presence of grinding balls (Fig. 6.3). The material is crushed as a result of the abrasion and impacts against obstacles in the drum, and the metallic component of the dross and the non-metallic components
Aluminium wastes are separated. The metallic part is processed in metallurgical plants, the non-metallic part is usually processed in the chemical industry.

B. The wet method
The procedure of the wet method of processing is as follows:
- crushing, sorting on sieves, magnetic separation
- leaching of crushed dross, thickening, filtration
- evaporation of the solution in furnaces in the fluid bed and gas purification
- washing and drying of the aluminium particles
- gas purification, and de-dusting.

![Aerofall mill](http://tera-3.us.cmu.edu/NASD/4dcb85c3-09ee-4c83-9e6d-fe6ce522e59/China/disk1/50/31006968/HTML/00000051.htm)

![Aerofall mill](http://www.outotec.com)

Fig. 6.3. Aerofall mill

- **Toxicity and ecotoxicity**

Aluminum is toxic for fish, which may show itself in acidified waters as a result of acid rainfall. Toxicity depends considerably on forms of aluminum occurrence. Aluminum is given into context with the Parkinson’s and Alzheimer’s disease (not proven, the Alzheimer’s disease destroys brain cells and the brain tissue shrinks, which results in a complex of functional problems and disorders).

### Sumary of terms

At the end of the chapter are repeated the main terms that you should acquire:

- **Wastes of aluminium and its alloys**
- **Processing of aluminium wastes and its alloys**
- **Processing of Al residues, dross, ashes**

### Question to the topic

1. What are the types of aluminium waste?
2. How are separated aluminium wastes?
3. What are methods of aluminium waste processing?
4. How do recycle Al residues, dross, ashes?

References


7. Wastes based on nickel

Study time: 3 hours

Objective After reading this paragraph, you will be able to
- define wastes of nickel and its alloys
- describe methods of nickel waste processing
- describe basic components of NiCd batteries and method of spent batteries recycling

Lecture

7.1 Nickel and nickel alloys

Nickel is metal with electrical conductivity (value corresponds to 25% copper conductivity). It is magnetic to 346 °C. It is a malleable metal, corrosion-resistant (resistant to alkalis). Nickel is resistant to atmospheric influences and water and therefore it is used as a thin nickel layer (nickel plating) on the surface less resistant metals. According to the technical classification of metals include nickel to the group of general (heavy) non-ferrous metals with medium melting point.

Properties:
- Symbol: Ni (Niccolum)
- Atomic weight: 58.71 g mol⁻¹
- Density: 8.90 g cm⁻³
- Melting point: 1453 °C
- Boiling point: 2730 °C

Application:
- an important element for alloying steels and non-ferrous metal alloys
- nickel plating - surface layer, protective layers
- as a catalyst (Raney nickel)
- in the form of chemical compounds for galvanic cells
- coinage metal.

Alloys:
- austenitic chromnickel steel
- stainless steel (up to 8% of Ni)
- heat-resistant steel (max. 2% Ni)
- permalloy - soft magnetic material (steel + up to 85% Ni)
- permanent magnets - steel with Ni, Co, Al
- Monel- stainless steel, 68% Ni and 32% Cu
- cupronickel - high corrosion resistance, high strength, 75% Cu and 25% Ni
- nickelin (30-35% Ni), constantan (42-35% Ni) – production of resistors and thermoelectric couples
- alloy Ni + Cr – resistance wires
- Nimonic (Ni-Cr 80/20) – materials with high strength in heat
- intermetallics – materials based on NiAl and NiTi, transition between metal and ceramic - high strength, but the disadvantage is its brittleness.
7.2 Characteristics of wastes based on nickel

According to ČSN 421331 standard, waste nickel and its alloys can be divided into:

- pure nickel waste incl. waste of nickel anodes from electrolytic baths
- low-alloy nickel waste
- nickel waste alloyed with iron, molybdenum, cobalt
- waste nickel alloyed with chromium
- waste nickel alloyed with copper
- nickel catalysts
- Ni-Fe batteries
- Ni-Cd batteries
- nickel residues - abradings, slag, electrolytic baths.

7.3 Processing of waste based on nickel

The processing of nickel waste depends on the nature of the feedstock. Nickel waste can be processed by means of pyrometallurgical process as well as hydrometallurgical process. When pyrometallurgical processing is used, nickel waste can be processed in two ways:

- processing nickel waste into ferronickel (a collective name for the alloys of iron and nickel, respectively other elements)
- common processing of nickel waste with the primary raw materials.

1. Processing of nickel waste into ferronickel

The charge used for melting into ferronickel contains various metal parts, either in the pure form or in alloyed one, as well as wastes in the form of chemical compounds (hydroxides, oxides, sulphates). The melt also includes soda, sodium hydroxide and carbon. The melting takes place in an electric arc furnace and is of reducing character. The melting process starts with the removal of moisture, decomposition of hydroxides and carbonates, followed by the subsequent reduction of the generated oxides.

2. Joint processing of nickel waste with the primary raw material

This method is sometimes undesirable (especially in case of oxidic ores) and is also used where nickel is produced only by melting and is not electrolytically refined. The undesirable element is especially antimony, which creates stable arsenides with Ni and Co. The separation of Sb from Ni is pyrometallurgically difficult. Melting is carried out in a shaft furnace, fine shares of Ni waste are briquetted, the individual components of the waste pass to gas, matte or slag. Fe from the waste acts as a reducing agent, otherwise iron in the form of pyrite is added as well. Melting waste in converters - the waste is added during the blowing of the nickel matte, when the nickel content rises to 40%. Cr, Mo and W pass into slag, and partly into flue dust emissions. Ni and part of Co from the waste sulphidizes and passes into matte.

3. Hydrometallurgical processing of nickel waste

This processing of waste is effective only when the waste has a higher content of Co. The impurities contained in the alloys are transferred into the solution together with Co or remain in the insoluble residue. During leaching in sulphuric acid, Fe, Al, Mn and Ni pass into the solution together with cobalt, and the insoluble residue contains W, Cr and Mo. The solvent is ferric sulphate, while the dissolution of cobalt and other metals is accompanied by the reduction of iron (Fe³⁺). The solution is transferred from the reactor part into a tank, where it is separated from sludge and subsequently pumped into the chlorinator for regeneration. The regenerated solution is reused for leaching.
4. Electrochemical methods used for dissolving waste with a high content of nickel

The waste is melted, followed by the casting of anodes which are anodically dissolved. Ni, Cr, and partially Mo pass into the solution. A larger proportion of Mo, W and Fe pass into sludge. The metals from the solution are obtained by extraction, hydrolysis, sorption, etc. The sludge is treated by sintering with soda in order to obtain W and Mo. This procedure is suitable for wastes with a higher nickel content.

7.3.1 Ni-Cd batteries

- **Functions and composition of Ni-Cd battery**

  **Nickel hydroxide** is the electrochemically active component of the positive electrode in the discharged state, and the active component of the negative electrode is represented by **cadmium hydroxide** (Fig. 7.1). The electrolyte is, in most cases, a solution of **KOH**.

![Fig. 7.1 Content and construction of NiCd battery](https://cactusbush.wordpress.com/tag/battery/)

Electrochemical processes during charging and discharging can be very simply described by the following equation 7.1:

\[
2 \text{Ni(OH)}_2 + \text{Cd(OH)}_2 \leftrightarrow 2 \text{NiOOH} + \text{Cd} + 2\text{H}_2\text{O} \quad (7.1)
\]

- **Processing of Ni-Cd batteries**

The facilities processing industrial NiCd and NiFe usually perform manual disassembly and sorting into components that are transferred to other companies, either as secondary raw materials for reuse or as waste for disposal. The materials from nickel and steel are transferred to the steel industry and the regenerated metal cadmium should be used for the production of new industrial batteries (Fig. 7.2).

We distinguish between two recycling processes:

- hydrometallurgical process
- pyrometallurgical process.
Hydrometallurgical process of recycling

Jedním ze způsobů zpracování je následující postup:

- the batteries are crushed, sorted and they are dissolved as a whole in a solution of HCl at higher temperature (90 °C)
- the removal of Fe and subsequent filtration leads to the extraction of CdCl₂ by means of tributyl phosphate
- followed by the re-extraction of cadmium chloride into a weakly acidic solution of HCl
- the pH adjustment with sodium hydroxide, when Fe precipitates as Fe(OH)₃ is followed by filtration
- the filtrate is used to obtain cadmium by means of electrolysis after the treatment
- the residue after extraction is subjected to pH adjustment with sodium hydroxide followed by the oxidation of NaClO forming Fe(OH)₃
- the adjusted solution is subsequently subjected to an Ni electrolysis.

Other suitable hydrometallurgical process is on Fig. 3.7 As the leach solution is used 20% solution of sulfuric acid.

Pyrometallurgical process of recycling

The separation of the electrodes from each other and their separate processing is an important prerequisite.

The individual electrodes are processed as follows:

- Ni electrodes for pyroreduction, i.e. for the production of nickel or NiFe alloy
- Cd electrodes are reduced with hydrogen or CO₂ into metallic cadmium
- in practice, a mixture of both reducing gases is used
- the reduction is followed by an oxidation back to CdO, which is isolated from the flue gases as powder, and it goes back to the production of Cd plates
- crystallization of Cd directly from the gas phase.

The technological procedure of processing of Ni-Cd batteries using SAFT-NIFE process is essentially a pyrometallurgical process.
Wastes based on nickel

Fig 7.3 Scheme of Cd, Ni recovery by hydrometallurgical processing of Ni-Cd batteries (RUDNIK, E., NIKIEL, M. Hydrometallurgy, 2007)

∑ Sumary of terms

At the end of the chapter are repeated the main terms that you should acquire:

Wastes of nickel and its alloys
Processing of nickel wastes and its alloys
Processing of Ni-Cd batteries

❓ Question to the topic

1. What are the types of nickel waste?
Wastes based on nickel

2. How are separated nickel wastes?
3. What are methods of nickel waste processing?
4. What are the basic components of NiCd batteries and how to recycle spent batteries?

References


8. Wastes containing precious metals

Study time: 2 hours

Objective
After reading this paragraph, you will be able to
- define wastes containing precious metals
- describe methods of processing of wastes containing precious metals

Lecture

8.1 Precious metals

The precious metals are metals, which are corrosion resistant, non-radioactive, expensive and rare and they have a high commercial value due to its specific characteristics. The basic characteristics noble metals are shown in Table 8.1.

The group of precious metals is, according to the technical classification of metals, divided into two basic groups:
- with a medium melting temperature: Ag, Au (precious metals)
- with a high melting temperature: Ru, Rh, Pd, Os, Ir, Pt (platinum metals, other precious metals).

These elements have a very high density, melting and boiling temperatures, and a low chemical reactivity. According to density, the platinum metals are divided into:
- light platinum metals (about 12 g·cm$^{-3}$) - ruthenium Ru, rhodium Rh, palladium Pd
- heavy platinum metals (about 22 g·cm$^{-3}$) - osmium Os, iridium Ir, platinum Pt.

![Fig. 8.1 Precious metals](http://clearscience.tumblr.com/image/1462372168)
Tab. 8.1 Characteristics of precious metals

<table>
<thead>
<tr>
<th>Element</th>
<th>Symbol</th>
<th>Temperature [°C]</th>
<th>Density [$\times 10^3$ kg·m$^{-3}$]</th>
<th>Group</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gold</td>
<td>Au</td>
<td>1064</td>
<td>19.32</td>
<td>with a medium melting temperature</td>
</tr>
<tr>
<td>Silver</td>
<td>Ag</td>
<td>961</td>
<td>10.49</td>
<td></td>
</tr>
<tr>
<td>Ruthenium</td>
<td>Ru</td>
<td>2334</td>
<td>12.45</td>
<td>with a high melting temperature - light platinum metals</td>
</tr>
<tr>
<td>Rhodium</td>
<td>Rh</td>
<td>1964</td>
<td>12.41</td>
<td></td>
</tr>
<tr>
<td>Palladium</td>
<td>Pd</td>
<td>1554</td>
<td>12.02</td>
<td></td>
</tr>
<tr>
<td>Osmium</td>
<td>Os</td>
<td>3033</td>
<td>22.59</td>
<td>with a high melting temperature - heavy platinum metals</td>
</tr>
<tr>
<td>Iridium</td>
<td>Ir</td>
<td>2446</td>
<td>22.65</td>
<td></td>
</tr>
<tr>
<td>Platinum</td>
<td>Pt</td>
<td>1768</td>
<td>21.45</td>
<td></td>
</tr>
</tbody>
</table>

Application / Consumption:
- Jewelry trade has the highest consumption of gold and photographic industry of silver. The highest consumption of platinum is in catalytic converters production for automobiles.
- Chemicals, dental applications and investments are the other main use of Ag, Au metals.
- Plating - jewelry, electric components, ...

Consumption of platinum metals, main application:
- Pd – 18.8 % electrical engineering, 50.5 % catalysts/catalytic converters, 10.8 % jewelry, 19.9 % other
- Rh – 81.3 % catalysts/catalytic converters, 1.0 % electrical engineering, 7.5 % glass, 7.5 % chemistry, 2.7 % other
- Ru – 8.8 % chemistry, 10.4 % electrochemistry, 74.9 % electrical engineering, 5.8 % other
- Ir – 20.2 % chemistry, 28.6 % electrochemistry, 21.0 % electrical engineering, 30.2 % other.

8.2 Wastes containing precious metals - characteristics

The examples of wastes containing precious metals are listed in Table 8.2; the marking is indicated according to the Catalogue of Waste.

Tab. 8.2 Examples of products containing precious metals (marking according to the Waste Catalogue)

<table>
<thead>
<tr>
<th>Type of waste</th>
<th>Code of waste</th>
<th>Name of waste</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electronic waste</td>
<td>20 01</td>
<td>Components from separand scrap collection</td>
</tr>
<tr>
<td></td>
<td>20 01 36</td>
<td>Discarded electrical and electronic equipment</td>
</tr>
<tr>
<td></td>
<td>16 02</td>
<td>Waste from electrical and electronic equipment</td>
</tr>
<tr>
<td></td>
<td>16 02 14</td>
<td>Discarded equipment</td>
</tr>
<tr>
<td>Dental metals</td>
<td>18 01</td>
<td>Wastes from natal care, from diagnostics, from treatment or prevention of human diseases</td>
</tr>
<tr>
<td></td>
<td>18 01 10*</td>
<td>Amalgam waste from dental care</td>
</tr>
<tr>
<td></td>
<td>18 01 03*</td>
<td>Wastes whose collection and disposal is subject to special requirements in order to prevent infection</td>
</tr>
<tr>
<td>Catalysts</td>
<td>16 08</td>
<td>Used catalysts</td>
</tr>
<tr>
<td></td>
<td>16 08 01</td>
<td>Used catalysts containing gold, silver, rhenium, rhodium, palladium, iridium or platinum (except for waste listed under number 16 08 07 - used catalysts contaminated with dangerous substances)</td>
</tr>
<tr>
<td>Photomaterials</td>
<td>09 01</td>
<td>Wastes from the photographic industry</td>
</tr>
<tr>
<td></td>
<td>09 01 01*</td>
<td>Aqueous solutions of developers and activators</td>
</tr>
<tr>
<td></td>
<td>09 01 04*</td>
<td>Setter solutions</td>
</tr>
<tr>
<td></td>
<td>09 01 06*</td>
<td>Wastes containing silver from the processing of photographic waste at the place of its origin</td>
</tr>
<tr>
<td></td>
<td>09 01 07</td>
<td>Photographic film and paper containing silver or silver compounds</td>
</tr>
</tbody>
</table>
8.3 Processing of wastes containing precious metals

The processing technology of waste precious metals can be divided into several processes:

- The process of direct remelting of wastes, which can include the reworking of jewellery and other jewellery products for new use.
- The process of direct processing of products in stomatology.

These processes are related only to direct remelting in the so-called goldsmith furnaces or in induction furnaces. Besides the aforementioned products, it is also possible to process spoiled goods from the production of these sectors. The melting process also takes advantage of sodium tetraborate as the covering salts.

Other sources of precious metals, which are subsequently processed by pyrometallurgical, hydrometallurgical or combined processes, include:

- waste from photographic industry - solid and liquid
- waste from electrical and electronic industry - manufacturing and discarded appliances
- catalytic converters
- telecommunication technology devices (mobile phones, telephone exchanges, etc.).
- catalysts
- coins
- other waste related to the processing of other wastes – e.g. anode mud.

Wastes containing silver

Production of silver from waste with a higher silver content

The following method has been developed to obtain silver from wastes containing a large amount of silver (e.g. old coins containing up to 50% of Ag): Silver alloy is diluted with copper in such a way to reduce the silver content in the alloy to 10 - 25%. The melt, which has been electrolyzed in sulphate electrolyte, is cast into anodes with the thickness of 5 mm. Copper dissolves and silver creates a rigid mould which is reprocessed to pure Ag.

Processing of anode mud

Copper can be characterized as the so-called collecting metal (collector) that is capable of concentrating precious metals into the melt during its pyrometallurgical production. These precious metals remain in copper until the last stage of processing, which is electrolytic refining. During the electrolytic refining, the undesirable elements or compounds remain dissolved in the solution in the form of anode mud (Fig. 4.13).

Anode mud is characterized as a mixture of oxides and sulphates of nickel, antimony, lead, tin and arsenic mixed with silver, gold and platinum group of metals. That is why this product is recognized as the most important source of precious metals (Fig. 8.2). The precious metal content is in the range of 6-20% Ag, 0.1 to 1.6% Au according to character of feedstock.

Fig. 8.2 Electrolytic silver and gold
Wastes containing precious metals

Wastes from photographic industry – solid and liquid photographic waste

1. Processing of solid wastes

Solid wastes from photographic industry include photographic paper, films, X-ray images, etc., which can be processed either with other metals which serve as collectors of precious metals, such as Pb, Zn, Cu and Fe, or these films can be processed separately. Scheme - the processing of silver during the production of lead. It should be noted that the processing product, i.e. raw silver, must be further refined.

Photographic film, papers and sludge are incinerated in batches in simple hearth furnaces, or they are continuously incinerated in rotary furnaces where they form ash rich in silver. The ash is processed with the other materials containing silver, the gases pass through a filter, and the dust is collected and treated as well in order to obtain silver.

Another method is the chemical separation of silver, where silver salt is leached from the emulsion layer. This process is used to process waste photographic film using sodium thiosulfate solution. Silver is electrolytically recovered from the leachate and the spent electrolyte is regenerated.

2. Processing of liquid wastes

Liquid wastes containing silver include especially developers, setters, washing waters, electroplating baths and other baths containing silver. Ag contents in some of the baths are as follows:

- spent setter solutions with a content of 60 - 90% of Ag
- washing solutions containing 10 - 40% of Ag
- photoemulsions with a minimum content of Ag.

The methods used to obtain Ag include:

- chemical precipitation
- cementation
- sorption and ion exchange
- cathodic reduction – electrolysis.

 Extraction of platinum, palladium and rhodium from catalytic converters

The platinum group metals ensure the transformation of harmful emissions into emission environmentally acceptable – Pt, Pd mainly carbon monoxide and Rh nitrogen oxides (Fig. 8.3).

Fig. 8.3 Principle and construction of catalytic converter

Types and characteristics of catalytic converters:
Catalytic converters are designed in three different types according to the type of ceramic or metal carrier (obr. 8.4):

- **Monoliths (ceramic),** the carrier part consists of honeycombed structure with a circular or elliptical cross-section from Fe-cordierite \((2\text{FeO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2)\) or Mg-cordierite \((2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2)\), which is coated with \(\gamma\)-alumina gel film containing precious metals. The average weight of the ceramic carrier is 900 g with the platinum content of 0.14 - 0.28 wt.% and rhodium content of 0.03 - 0.05 wt.%.
- **The metal carrier** has the so-called honeycomb structure made from a thin corrugated foil of high alloy steel (Ni-Cr tape), which is rolled into the shape of letter "S". A porous interlayer of \(\text{Al}_2\text{O}_3\) (modification of \(\gamma\)) is coated on the metal walls.
- **Pellets,** the carrier part consist directly of \(\gamma\)-alumina. The weight of the pellets is about 2.5 kg, they have spherical or cylindrical shape with a diameter of 3 - 12 mm. Nowadays, the simplest type is virtually not used anymore.

![Fig. 8.4 Catalytic converters: monolithic, metal carrier rolled into the shape of letter "S"](image)

![Fig. 8.5 The general technological procedure of recovery precious metals from catalytic converters](image)
Technological methods of recycling Pt, Pd, Rh

There are several ways of retrieving precious metal catalysts from discarded catalytic converters. The general technological procedure is schematically illustrated in Figure 8.5.

Hydrometallurgical recycling methods

In case of hydrometallurgical processing, the precious metals are leached with strong acids and the leachate containing precious metals is subsequently purified by means of chemical precipitation or cementation. Pure leachate is further processed into metal, into chemical concentrate of precious metals, or it is processed using special methods (adsorption, ion exchange, extraction). Platinum metals are retrieved from monolithic catalysts, whose carrier part consists of Fe-cordierite or Mg-cordierite with a gel coating of γ-alumina with precious metals using the following method: After the mechanical treatment of the catalyst (crushing), γ-alumina is dissolved in sulphuric acid. After decantation, the undissolved residues containing mainly platinum metals are dissolved by HCl + Cl₂. Part of platinum metals, which passed into the solution, is obtained by precipitation of Al with the presence of tellurium dioxide. The following part is the reduction of platinum metals using sulphur dioxide (Te as the collector.) The resulting suspension is hot-filtered and, after cooling, the lead chloride if filtered off and HCl is recycled. The platinum metals are readily soluble in HCl + Cl₂, because the volume of the solution is small and the concentration of the platinum metals is high. The raffinate containing concentrated platinum metals (platinum metal halides) is used directly for further separation. Tellurium compounds are extracted by means of tributyl phosphate and they are returned back into the process after reextraction.

Pyrometallurgical recycling methods

Pyrometallurgical recycling methods focus mainly on melting copper as the collection metal and on plasma melting technology, which mostly uses iron as the collector. They are more energy intensive than the hydrometallurgical methods.

When recycling the catalyst by means of plasma melting, the catalyst is crushed and ground and subsequently mixed with Fe + FeO, and the resulting mixture is melted in a plasma furnace at a temperature exceeding 2 000 °C. The mixture is maintained in molten state for some time in order to separate the light layer of molten slag and the heavier phase containing Fe with platinum metals. Fe alloy is dissolved in sulphuric acid. Undissolved platinum metals are filtered out and the filtrate is neutralized.

During melting with copper, the catalyst after mechanical treatment involving crushing and grinding, together with cupric carbonate, silicon dioxide (silica), calcium oxide (lime) and ferrous oxide (wüstit), is melted in a special electric furnace at temperatures of 1600 – 1800 °C. The melt is divided into slag and an alloy of platinum metals with copper. The copper alloy is dissolved in an aqueous sulphuric acid solution using air as the oxidant. Copper is obtained by means of precipitation using soda ash as the basic carbonate. The cooled solution is filtered. The entire process is carried out in such a way to recycle copper.

Combined recycling methods

The chlorination of catalyst is a combined method of recycling of precious metals. The catalyst is calcined, the platinum metals are reduced and chlorinated by means of NaCl at high temperatures. They are subsequently leached with water and extracted from the solution. The crushed catalyst is mixed with sodium chloride. The mixture is calcined to remove the organic impurities and carbon black. This is followed by the reduction of oxides of platinum metals with carbon monoxide and, after that, the reactor is charged with chlorine and maintained at the temperature of 600 - 700 °C. After partial cooling, the reactor is washed with hot water, the platinum metals are reduced from the solution using sulphur dioxide in the presence of tellurium dioxide. Filtration at higher temperatures produces platinum metals, while lead chloride is isolated from the filtrate.
The yields of the presented recycling methods

Spent catalytic converters may contain an average of 1000 grams of platinum metals per 1 ton of processed material. Each of these recycling methods has its advantages and disadvantages. The yields of platinum metals from the individual recycling processes are different as shown in Table 8.3.

<table>
<thead>
<tr>
<th>Process</th>
<th>The yield [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pt</td>
</tr>
<tr>
<td>Acid leaching</td>
<td>88 - 94</td>
</tr>
<tr>
<td>Dissolution of monoliths</td>
<td>85 - 92</td>
</tr>
<tr>
<td>Chloration</td>
<td>85 - 90</td>
</tr>
<tr>
<td>Plasma melting</td>
<td>80 - 90</td>
</tr>
<tr>
<td>Melting - Cu collector</td>
<td>88 - 94</td>
</tr>
</tbody>
</table>

Sumary of terms

At the end of the chapter are repeated the main terms that you should acquire:

- Wastes containing precious metals
- Processing of wastes containing precious metals
- Recycling of photographic waste containing silver
- Recycling of catalytic converters

Question to the topic

1. What are the wastes containing precious metals?
2. How are processed precious metal wastes?
3. What are methods of silver containing waste processing?
4. What are the basic components of car catalytic converter and how to recycle spent converters?

References

9. Electrical and electronic waste

Study time: 2 hours

Objective After reading this paragraph, you will be able to
• define waste electrical and electronic equipment
• characterize e-waste
• describe methods of processing of electronic wastes

Lecture

9.1 Waste electrical and electronic equipment

Electrical and electronic waste
Waste of electrical and electronic equipment (WEEE, abbreviated as e-waste) such as computers, printers, photocopiers, TV-sets, fridges and cell phones is one the fastest growing waste streams in the EU, with some 9 million tonnes generated in 2005, and expected to grow to more than 12 million tonnes by 2020. High production of e-waste is a global problem (Fig. 9.1).

Waste electrical and electronic equipment (WEEE) belongs to wastes containing a wide range of metals, namely light metals (Al), heavy metals (Cu, Ni, Pb, Sn) and a number of precious metals (Ag, Au, Pt, Pd) and others.

Their processing technologies are complicated and during the first stage they include manual dismantling, crushing and separating polymers from the metal fraction followed the processing of the metals by means of pyrometallurgical, hydrometallurgical, or combined technologies.

9.2 Characteristics of e-waste

„Waste electrical and electronic equipment” (WEEE) is electrical and electronic equipment which represents waste.

In a simplified definition, e-waste is electrical equipment which has become waste, including all the components, subassemblies and consumables which are part of the equipment at that moment.


1. Large household appliances
2. Small household appliances
3. IT and telecommunications equipment
4. Consumer equipment
5. Lighting equipment
6. Electrical and electronic tools (with the exception of large-scale stationary industrial tools)
7. Toys, leisure and sports equipment
8. Medical devices (with the exception of all implanted and infected products)
9. Monitoring and control instruments
10. Automatic dispensers

Nowadays, the recycled components from electrical and electronic scrap include ferrous metals (iron, cast iron, steel), non-ferrous metals (Cu, Al, Pb, Sn, Ni, Zn), noble metals (Au, Ag, Pt, Pd, Se, Te, Ga, In) and pure homogeneous plastics, rubber and glass.
Fig. 9.1 World production of E-WASTE

9.3 Processing of e-waste

The waste is sorted into the basic components of the same type of materials, such as metals - ferrous and non-ferrous, plastics, motherboards and printed circuits, cables and wires and other components represented to a lesser extent. Examples of the basic components of different kinds of materials are shown in Fig. 9.2.
Recycling processes

The recycling process should include the following steps:

Material assessment
- assessing the residual value by a business partner is particularly important for estimating the economic contribution of recycling
- the evaluation of electrical waste made by the processor with respect to the best possible method of processing

Added value
- reuse and sale of goods to a third party
- reconstruction, modernization of goods for sale or donation to a third party

Pretreatment
- removal of the individual parts for reuse
- disassembly for the purpose of recycling or removal of harmful or valuable components
- processing by grinding, milling, granulating, cutting, packeting, briquetting, by means of cryogenic methods
- separation of ferrous and non-ferrous shares, noble metal, plastics etc.

Metal recycling
- iron smelting
- refining of non-ferrous metals

Processing (disposal)
- recycling of hazardous substances
- disposal of hazardous substances

Depositing
- deposit of hazardous components
- deposit of non-recyclable electrical waste residues.
Methods of recovery of the individual components of electrical waste

The structure of electronic waste has been constantly changing. E-waste material composition is diverse, this waste contains many valuable materials. An example of material content is given in Fig. 9.3.

![Composition of E-waste](image)

**Fig. 9.3 E-waste material composition**  

There is an increasingly stronger demand for improvement and effective stimulation of waste collection methods and in particular for a strict separation of the individual fractions.

The individual methods of electrical waste processing can be divided as follows:

- mechanical methods
- pyrometallurgical methods
- hydrometallurgical methods
- electrochemical methods
- biotechnological methods.

**Mechanical methods**

The first operation in case of electronic waste, prior to mechanical processing, is usually manual or partly mechanized dismantling focused on the components containing precious metals, such as transformers, coils, cooling elements, engines, condensers, batteries, cables, circuit boards, motherboards etc. (Fig. 9.4).

Manual work is also required to remove the components containing hazardous substances, e.g. mercury switches, batteries, condensers containing PCB (polychlorinated biphenyls).

Typical technologies used during the mechanical processing of electrical waste are:

- manual dismantling
- crushing, grinding, sorting
- separation of the individual components
- refining.

**Manual dismantling**

- disassembly of contacts containing noble metals and the removal of printed circuit boards
- the removal of components containing hazardous metals
- the removal of screens from monitors.
Electronic waste

**Crushing, grinding and sorting**
- the used shredders, mills and sorting machines vary depending on the capacity, fraction coarseness and the amounts of processed scrap
- the lines usually include a shredder followed by a mill.

**Separation of the individual components**
A mixture of the shredded materials is divided into the individual fractions - plastics and metals are separated by different technologies:
- cryogenic technologies used for sorting and separation of various metals
- heating in order to obtain low-melting metals contained, eg., in solders
- magnetic separation to separate metals from plastics
- air separation used to separate plastics from metals
- heavy-suspension separation, sorting of different metals according to their density
- electromagnetic separation of various non-ferrous metals.

**Refining**
- removing undesirable impurities from the final product.

---

**Electronic Waste Recycling**

![Diagram of Electronic Waste Recycling](http://www.appropedia.org/Metal_reclamation_and_recycling_of_electronic_waste)

Fig. 9.4 Electronic waste recycling
Pyrometallurgical methods

When pyrometallurgical methods are used, electronic waste can be processed directly, but the first step is usually mechanical treatment. Pyrometallurgical processes are applied similarly as in processing of intermediate products containing precious metals.

The pyrometallurgical processes are:

- **pyrolysis**
- **melting**:
  a) melting in a flame furnace, where the polymers are burnt at 400 °C followed by melting at a higher temperature, we obtain copper ingots that are refined
  b) melting collected metal – electrical wastes can be melted simultaneously with the primary feedstock or separately in a shaft furnace together with the refining wastes; melting of selected types of electrical wastes (printed circuit boards) with lead as the collecting metal in a shaft furnace.
- **sintering**
- **reaction with the gas phase at high temperatures** - this procedure is used for processing of crushed gilded electronic components. It uses the potential formation of AuCl₃ by the action of chlorine gas at the temperature of 500 °C.

Hydrometallurgical methods

Hydrometallurgical processes are among the most widespread methods of processing of waste from electronic and electrical industries.

This processing extensively uses the mechanically pre-treated materials, where the metals are concentrated up to a specific share.

The following operation is leaching using a suitable leaching agent.

The most frequently processed leach is the one with high metal content.

Hydrometallurgical processing usually takes place in several stages. We distinguish the following types of leaching:

a) acid leaching
b) alkaline or ammoniacal leaching
c) combined.

The subsequent processing into metal or a chemical concentrate is carried out by:

a) cementation,
b) precipitation,
c) distillation precipitation,
d) ion exchange,
e) extraction,
f) extraction electrolysis.

∑ Sumary of terms

At the end of the chapter are repeated the main terms that you should acquire:

Waste of electrical and electronic equipment (WEEE, e-waste)
Processing of e-waste
Methods of recovery of the individual components of electrical waste
Question to the topic

1. What is e-waste?
2. How are processed e-wastes?
3. What are methods of e-waste processing?

References


10. Tin and tin-plated wastes

Study time: 2 hours

Objective  After reading this paragraph, you will be able to

- define waste of tin and its alloys
- describe methods of tin and tin-plated waste processing

Lecture

10.1 Tin and tin alloys

Tin is well ductile and corrosion resistant metal. Metallic tin is resistant to acids, which are used in iron protecting against corrosion, e.g. in the production of food cans. According to the technical classification of metals include tin to the group of general (heavy) non-ferrous metals with low melting point.

Properties:
Symbol            Sn (Stannum)
Atomic weight     118.69 g·mol⁻¹
Density           7.30 g·cm⁻³
Melting point     232 °C
Boiling point     2270 °C

Application:
Tin is used in many technical applications. The biggest share is consumed by the solder and tinning (Fig. 10.1). Tin has been used as metal since the ancient times (tin bronze), but its use has recently been restricted due to the fact that it is one of the most deficient metals. Its use, however, is in many cases unavoidable, and it is most often used as a protective coating in the produce of tin plate, in production of solders in electrotechnical industry, in the produce of tinned wires and slide bearings.

Industry consumption 2011

<table>
<thead>
<tr>
<th>Market Sector</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solder</td>
<td>52</td>
</tr>
<tr>
<td>Tinplate</td>
<td>17</td>
</tr>
<tr>
<td>Chemicals</td>
<td>15</td>
</tr>
<tr>
<td>Brass &amp; Bronze</td>
<td>5</td>
</tr>
<tr>
<td>Glass</td>
<td>2</td>
</tr>
<tr>
<td>Others</td>
<td>10</td>
</tr>
</tbody>
</table>

Source: ITRI-CRU www.itri.co.uk, www.crugroup.com

Fig. 10.1 Consumption of tin
Organic compounds of tin are used as catalysts in the chemical industry (production of polyurethane), as stabilizers in the production of plastics (PVC stabilization), as well as pesticides.

- **The advantages of using tin**
  - hygienic safety
  - corrosion resistance to weathering and water
  - resistance to organic compounds in foods
  - low melting point.

**10.2 Tin wastes**

According to ČSN 421331 standard, tin wastes can be divided into:

- pure tin waste containing at least 98.0% of Sn
- Sn bearing alloy wastes (Sb, Cu, Ni, Pb)
- waste of tin alloys (Sn max. 98.0%)
- tin and tin alloy residues
- unsorted tin and tin alloys wastes.

**Waste tin-plated sheet metal**

Tin-plated sheet metal, the so-called tin plate, is a valuable source of secondary tin. The remains of tin plates and waste tin-cans are good sources of tin, since it is a valuable raw material, but it is also necessary to remove a substantial part of tin protective layers from the surface of steel sheets. When processing this type of waste, it is first necessary to remove the tin from the surface of tin plate (tin-cans) and the iron waste after the removal of tin is used as scrap in the production of iron and steel.

**10.3 Tin waste treatment processes**

We can recycle all pure tin wastes, tin alloy and wastes containing minor fractions of Sn (tin plate cuttings, used tin-cans, slag, dross, ....). Lump tin waste is easy to recycle - to remelt and to refine. If the waste also contains lead and other impurities, it is easier to prepare Sn-Pb alloy (solder alloy). There are several processing techniques used for the processing of tin plate waste.

Old metals and metal wastes containing mainly tin and lead are not processed into pure tin, but into alloys with 50 or more percents of tin (the rest consists of lead, antimony and copper - it's the so-called mixed tin). This way is used to remelt the waste of anti friction alloys, solders and type metal. Mixed tin is used to manufacture solders with a content of tin lower than 50% and inferior alloys. Alloys with higher tin content are remelted in flame furnaces and then they are segregated. The processing of these wastes into pure tin is technically possible, but it is so expensive due to large losses of tin that it is more profitable to produce alloys or, in extreme cases, to produce raw tin with a maximum Sn content of 95%.

**10.4 Recycling of tinplate waste (from food industry)**

There are a number of processes used for the processing of tinned waste. 70% of the total amount of produced tinplate is used for making tin-cans, the rest is used for other applications. The production of tin-cans generates waste in the form of segments, and cuttings in the amount of app. 20%. The mean Sn content is about 0.95 to 1.2%. The usable tin content from the used tin-cans is, however, significantly lower. Other tin dissolves in the foodstuffs during storage. The amount of tin is also reduced due to the formation of an interlayer of FeSn2 (5-10% Sn). The total irretrievable losses of Sn are 20-25% of the total amount of Sn coating. The presence of surface varnishes can be problematic during the waste processing.

- **The possible methods of tin plated waste processing**
  Tin has recently been acquired from tin plate, especially electrolytically. The used method is based on leaching in alkaline environment. Tin from tin plate is successfully obtained thanks to the effect
Tin wastes

of chlorine, where completely dry chlorine gas is fed at a low temperature (forced cooling) and under pressure to tin plate cuttings pressed into bales (for easier placing into open-hearth furnaces for further processing). Chlorine mixes with tin into SnCl₄ (liquid at room temperature), which is discharged. Unless the chlorine is dry, iron melts as well, which is not desirable. The resulting stannic chloride is used directly or it is processed into metallic tin.

Processing methods:
1. Using a higher temperature (the so-called cupellation) – it takes place at a temperature of 350 °C, the process may be used if there is a large Sn layer.
2. Mechanical methods (sanding).
3. Chlorinating method.
4. Hydrometallurgical processes (acidic or alkaline solutions).
5. Electrolytic processes (with acidic or alkaline solutions).

Chlorinating method

The fundamental reaction during the chlorination process is the reaction with chlorine gas into tin tetrachloride, which is a colourless fuming liquid with a melting temperature of 33.0 °C and a boiling temperature of 113.9 °C:

\[ \text{Sn} + 2 \text{Cl}_2 = \text{SnCl}_4 \]

The necessary processing condition - complete removal of moisture from the waste, because otherwise it leads to the dissolution of the steel base and the contamination of tin tetrachloride according to the reactions:

\[ \text{Cl}_2 + \text{H}_2\text{O} = 2 \text{HCl} + \frac{1}{2} \text{O}_2 \]
\[ \text{Fe} + 2 \text{HCl} = \text{FeCl}_2 + \text{H}_2 \]
\[ \text{H}_2 + \frac{1}{2} \text{O}_2 = \text{H}_2\text{O} \]

Another condition is the removal of organic substances – they are dissolved in SnCl₄ and they pollute it. The chlorination is carried out in cylindrical retorts with the diameter of 3 m and the height of 5 m. The charge consists of 12 to 15 tons of waste containing 300 kg of tin. The chlorination takes place at a temperature of 38 °C, and the chlorination time is 8-10 hours, the liquid SnCl₄ collects at the bottom of the retort. The resulting SnCl₄ removes iron by means of distillation. It can be processed into metallic tin or tin salts. Tin can be produced from chloride by means of electrolysis or by cementation.

Hydrometallurgical processes (acidic or alkaline solutions)

1) Acidic solutions are not used due to the fact that they also attack the steel base and have a high consumption.

2a) Alkaline - NaOH solution, the reaction is intensive in the presence of oxygen leading to the formation of sodium stannate:

\[ 2 \text{NaOH} + \text{Sn} + \text{O}_2 = \text{Na}_2\text{SnO}_3 + \text{H}_2\text{O} \]

Without the presence of oxygen, it leads to the formation of sodium stannite (Na₂SnO₃), the reaction is slow.

2b) Instead of oxygen, it is possible to use another oxidizing agent - lead acetate, respectively PbO Pb(C₂H₃O₂)₂, PbO, NaNO₃, air:

\[ \text{Sn} + 2 \text{PbO} + 2 \text{NaOH} = \text{Na}_2\text{SnO}_3 + \text{H}_2\text{O} + 2 \text{Pb} \]
\[ 4 \text{Sn} + 6 \text{NaOH} + 2 \text{NaNO}_3 = 4 \text{Na}_2\text{SnO}_3 + 2 \text{NH}_3 \]

The above presented procedures using oxidizing agents are not widely applied because of the complicated technologies and a large consumption of the oxidizing agents.

Tin can be removed from stannate solutions by means of:
Tin wastes

- **electrolysis** with insoluble anodes
- precipitation using CO\textsubscript{2}
  \[
  \text{Na}_2\text{SnO}_3 + \text{CO}_2 = \text{SnO}_2 + \text{Na}_2\text{CO}_3
  \]
- precipitation using NaHCO\textsubscript{3} or Ca(OH\textsubscript{2})
  \[
  \text{Na}_2\text{SnO}_3 + 2 \text{NaHCO}_3 = \text{SnO}_2 + \text{Na}_2\text{CO}_3 + \text{H}_2\text{O}
  \]
  \[
  \text{Na}_2\text{SnO}_3 + \text{Ca(OH)}_2 = \text{CaSnO}_3 + 2 \text{NaOH}
  \]
- acids
  \[
  \text{Na}_2\text{SnO}_3 + \text{H}_2\text{SO}_4 + \text{H}_2\text{O} = \text{Sn(OH)}_4 + \text{Na}_2\text{SO}_4
  \]

3) **The processing of tin plates by means of alkaline leaching in the presence of organic oxidizing agents**

The advantage of using these organic agents is their regeneration. The used agents are:
- metanitrobenzene acid
- trinitroptalene acid
- meta nitrobenzene sulphonic acid.

**Electrolytic detinning**

Tin has recently been obtained from tinplate by means of an electrolytic method, although it is more expensive than detinning using chlorine. Tinned industrial wastes (sheet cuttings, ...) and used tin cans are suspended in iron cages to 9-10% sodium hydroxide solution and they are electrolyzed at a temperature of 70-85 °C and a voltage of 1.5 V. The waste is connected as an anode, pure steel sheets as a cathode. Powder tin is depositing on the cathode with the purity of 95 to 97%, and it is remelted after peeling of. It usually contains 2-3% of lead and iron. The Figure 10.2 shows a scheme of electrolytic detinning of tinned waste.

Electrochemical oxidation of solid tin **on the anode:**

\[
\text{Sn (s) + 2 H}_2\text{O (l) = HSnO}_2 (aq) + 3 H^+ + 3 e^-}
\]

Depositing of solid tin **on the cathode:**

\[
\text{HSnO}_2 (aq) + 3 H^+ + 3 e^- = \text{Sn (s) + 2 H}_2\text{O (l) }
\]

![Scheme of electrolytic detinning of tinned waste](http://www.doitpoms.ac.uk/tlplib/recycling-metals/tin_cans.php)

Fig. 10.2 Scheme of electrolytic detinning of tinned waste
Metallic tin is depositing much faster than iron, iron under the right circumstances is passivated, which means it does not corrode (does not dissolve). The steel cathodes surround the cages. Powder tin is depositing on the cathode. The main source of income for the processing companies is the sale of detinned scrap metal. Max. permissible Sn content for further processing of Fe waste in steel plants after detinning is 0.05 to 0.06 vol.%. 

10.5 Toxicity of tin

Tin is a trace element, for which no specific biochemical function has been clearly identified to date. Some studies state that tin is an essential trace element, nevertheless, it has been proven that organic compounds of tin are toxic. Increased doses of Sn have toxic effects.

At ingestion, tin toxicity level is mild, partly due to its poor absorption and low retention in tissues. Metallic Sn is only slightly toxic, in contrast to highly toxic organic compounds (mainly organostannic compounds). Chronic exposure to tin may cause retardation of growth and anemia. The increased Sn intake influences the activity of many enzymes and it is assumed that metabolism of Zn, Cu and Ca may be affected as well. Higher toxicity can be found at intake of organic tin compounds, which attack the central nervous system. Changes in the myelin and spongiform degeneration of brain occur, which shows itself as ataxia and a complete paralysis may occur and even death.

∑ Sumary of terms

At the end of the chapter are repeated the main terms that you should acquire:

Wastes of tin and tin alloys
Processing of tin waste
Tin-plated waste, white plate
Processing of tin-plated waste

❓ Question to the topic

1. What are tin wastes?
2. What are methods of tin waste processing?
3. What are methods of detinning?

References

11. Wastes of zinc and its alloys

**Study time:** 2 hours

**Objective** After reading this paragraph, you will be able to

- define zinc and its alloys
- describe methods of zinc and zinc-coated waste processing

**Lecture**

11.1 Zinc and its alloys

Pure zinc is used for zinc coating of semifinished products (tubes, wires, sheets) as a protective layer against corrosion. Zinc compounds are very important as well, for example ZnO is widely applied in the manufacture of coatings and in rubber industry. Zinc alloys are used for foundry purposes, because they have excellent castability and better strength properties than pure zinc. Zinc is resistant to petrol, alcohol, slightly alkaline solutions. Is resistant to corrosion in air, it is covered with a layer of basic carbonate, in water of normal hardness is resistant, in distilled water is subject to corrosion, water vapor significantly damaging it. Zinc is well thermoformable and can be easily. According to the technical classification of metals include zinc to the group of general (heavy) non-ferrous metals with low melting point.

**Properties:**

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Symbol</td>
<td>Zn (Zincum)</td>
</tr>
<tr>
<td>Atomic weight</td>
<td>65.38 g·mol⁻¹</td>
</tr>
<tr>
<td>Density</td>
<td>7.13 g·cm⁻³</td>
</tr>
<tr>
<td>Melting point</td>
<td>419.5 °C</td>
</tr>
<tr>
<td>Boiling point</td>
<td>906 °C</td>
</tr>
</tbody>
</table>

**Application:**

Zinc is well thermoformable and is easy to cast. The most significant Zn alloys include Zamak, where the main alloying elements are Al and Cu. These alloys are largely used for casting under pressure. Zinc is widely used as an alloying element for the production of alloys (brass, red bronze with content of Zn 2-6 %). A large part of the zinc is used for galvanizing.

- **Zinc coating**

Zinc coating - a process ensuring the protection of the base metal (iron) against corrosion. Zinc coating is the most commonly used process in the field of corrosion protection of all the processes. We distinguish two types of zinc coatings, **zinc dipping and zinc plating**.

11.2 Zinc wastes

Zinc wastes may be in the form of lump waste, remains, and the sources of secondary zinc also include waste zinc coated iron or steel sheets.
According to ČSN 421331 standard, zinc wastes can be divided into:

- waste of pure zinc containing min. 98.5% of zinc
- mechanically polluted zinc waste containing min. 98.5% of zinc
- waste Zn formed and foundry alloys
- waste Zn formed and foundry mechanically polluted alloys
- Zn from zinc coating baths (Zn min. 90 %)
- remains of Zn and Zn alloys (Cl max. 3 %)
- remains of Zn and Zn alloys (Cl more than 3 %)
- unsorted Zn and Zn alloys wastes.

Types of zinc residues

Hard zinc - consisting of about 90% of Zn, 8% of Fe, and impurities. Most of hard zinc is produced during zinc dipping.

Zinc ash – produced during melting of zinc and its alloys and during dry zinc coating. Apart from oxidic zinc, it contains the remains of 10-15% of metallic zinc.

Ammonium chloride skimmings - formed during the wet tin coating process. Untreated ammonium chloride skimmings contain 18 to 22% of metallic zinc, 30-35% of ammonium chloride and zinc chloride, 30-35% of zinc oxide, 10-20% of iron oxide. They must be stored separately.

Pure zinc waste - sheets, chips, graphics, etc.

11. 3 Zinc waste treatment processes

All zinc waste (pure zinc, zinc alloys, zinc coated scrap and Zn residues) can be recycled. Galvanized sheet scrap is melted together with the iron scrap in the production of steel and zinc is recovered from the dust fraction.

Processing of lump zinc waste

Lump waste is processed by remelting in steel pots or flame furnaces. The depth of the steel pots exceeds their diameter approximately twice. This is important for the removal of lead and iron, which are separated from zinc on the basis of limited solubility and different densities.

Recovering zinc from zinc residues

Processing of hard zinc

This type of waste is processed using different processes - production of lower quality zinc white, or it can be used in distillation furnaces, part of the zinc can be obtained directly from hard zinc by means of segregation in pots or in flame furnaces with inclined hearth at about 450 °C.

Segregation in deep kettles - the temperature is maintained at the level of 475 °C, and it must be as low as possible at the bottom. Hard zinc, which melts at 450-600 °C, is collected at the bottom of the pot; pure zinc can be discharged after some time from the upper part.

Segregation in hearth furnaces with an inclined bottom (450 °C) – used to process, e.g., the rest of hard zinc after segregation in pots in order to obtain the highest possible share of pure Zn. The rest of hard zinc is subsequently reworked into zinc white or zinc dust (the same procedure as in case of EAF dust).

Zinc may be refined from iron by the addition of aluminium - this transfers Fe into intermetallic phase of Fe-Al, which floats on the bath surface. Recycling zinc from galvanized sheets

The presence of the zinc coating on steel does not limit the recyclability of steel and all types of zinc coated steel products are recyclable. Galvanized steel is recycled along with other types of steel scrap during the production of steel – zinc evaporates during remelting, it is collected on separators and the collected dust is recycled. The ratio of the charge material and the obtained products is shown in Fig. 11.1.
Processing method:

**Remelting in an electric arc furnace and reworking into zinc white**

The most commonly used method of galvanized steel recycling is remelting in an electric arc furnace. High temperatures cause the evaporation of zinc - volatile zinc in the form of vapour leaves the furnace together with other gases. The gas stream is discharged through a filter - the so-called zinc dust (EAF dust), which contains 18-35% of Zn, is caught and the main component is iron.

This dust is processed by the so-called Waelz process in rotary furnaces. The product is zinc oxide (Waeltz Oxide) = zinc white, which is a valuable raw material, or it is further processed in order to produce metallic zinc (Fig. 11.2).
Processing of zinc dust in rotary hearth furnaces

Another possible way of EAF zinc dust reworking into zinc white is the processing technology taking advantage of a rotary hearth furnace (Fig. 11.3). Zinc dust is mixed with finely ground coke and briquettes are produced. These are then used as charge into a rotary hearth furnace, where the charge is heated, leading to the evaporation of zinc. Zinc vapours are captured and cooled. Zinc concentrate is further processed. The residual ferrous share is briquetted.

11.4 Toxicity of zinc

Zinc belongs to essential elements, a certain specified concentration is essential for humans. A deficiency of zinc may cause neuropsychological abnormalities, dermatitis and malfunction of the immune system. However, a high concentration of zinc may result in health problems. Inhalation of zinc oxide fumes is associated with the so-called metal fume fever (fatigue, headaches, cough, high temperature, proteins in urine). Soluble zinc salts are toxicologically more significant – zinc sulfate heptahydrate (white vitriol) and zinc chloride.

Σ

Summary of terms

At the end of the chapter are repeated the main terms that you should acquire:

Wastes of zinc and zinc alloys
Processing of zinc-coated waste

Question to the topic

1. What are zinc wastes?
2. What are methods of zinc waste processing?
3. What are methods of recycling zinc from zinc-coated sheets?
References


12. Wastes containing mercury

Study time: 2 hours

Objective  After reading this paragraph, you will be able to

- define wastes containing mercury
- describe the technologies of waste demercuration

Lecture

12.1 Mercury

According to the technical classification of metals include mercury to the group of general (heavy) non-ferrous metals. This metal is in the liquid state at normal temperature. It is remarkably weight and it has good electrical conductivity. The most important practical application has mercury in the form of their alloys with other metals - amalgams. Mercury reacts with Ag, Au, Cu, Zn, Cd, Na, while with iron metals such as Fe, Ni and Co does not react.

Properties:

Symbol: Hg (Hgdraryrum)
Atomic weight: 200.59 g·mol\(^{-1}\)
Density: 13.56 g·cm\(^{3}\)
Melting point: -38.84 °C
Boiling point: 356.9 °C

Application:

Mercury belongs to the elements whose effect on the human organism is clearly negative. MERCURY IS HIGHLY TOXIC. The most important practical application of mercury is in the form of its alloys with other metals - amalgams. It is easy to make alloys with Au, Ag, Cu, Zn, Cd, Na, while they are not created at all with iron metals, such as Fe, Ni and Co. At present, mercury is mainly used for the production of industrial chemicals (in the production of chlorine, soda and NaOH). Lamps containing mercury (fluorescent tubes, mercury lamps) have a higher luminous efficiency than conventional bulbs with tungsten filament. It is included as an antibacterial and antifungal additive in coatings.

12.2 Wastes with mercury

A considerable part of waste materials containing mercury belongs to hazardous wastes.

According to ČSN 421331, mercury and mercury alloy wastes have the designation class of 961.

Wastes containing mercury:

- fluorescent tubes
- halogen lamps
- batteries containing mercury (button cells)
- electrical appliances, e.g. switches and rectifiers
- manometers
Wastes containing mercury

• mercury thermometers
• medical materials (from nuclear medicine, dental waste)
• sediment and filtering equipment
• catalysts
• military material
• wastes from various industrial technological processes
• others.

12. 3 Treatment processes of waste containing mercury

When processing waste containing mercury, it is necessary to perform this work under higher security measures. The basis of processing technology is a distillation of mercury in distillation plant.

☐ System MRT

Processing of waste containing mercury is performed, for example, by a Swedish company MRT. There is an established recycling technology used to process fluorescent tubes - MRT system with several possible processes for the separation of the individual components.

MRT system consists of two technology nodes:
1. mechanical preparation of waste - two methods:
   • Kapp method
   • Shreder method
2. the recycling technology itself.

1. Mechanical preparation of waste

Kapp method - it is beneficial for the processing of long fluorescent tubes:
• separation of screw caps by means of "end cut and separate" method – cutting off the ends
• blowing off luminophores from the fluorescent tubes
• sucking off luminophore powder containing mercury
• glass is crushed and we obtain glass of high purity (the best method meeting the request for high purity of the secondary glass)

Shreder method – suitable for all fluorescent tubes and bulbs, processing in vacuum containers, the equipment is absolutely compact:
• crushing
• separation of glass from the metal parts
• sucking off the luminophore powder.

2. Recycling technology

The actual recycling takes place after the mechanical preparation – final sorting and separation of the individual material components - glass, metal fraction, luminophore powder. Luminophore powder is separated in a special air-cleaning device. Distilling off the mercury is carried out at a temperature of about 700 °C. Mercury is discharged in the form of vapours, which pass into the condensation system where they are cooled and mercury is condensed in liquid form (Fig. 12.1). Generally, this procedure of the removal of mercury can be used for most mercury-containing wastes. After the removal of mercury, the waste can be transferred to other processors or it can be directly supplied as a secondary raw material for further production (glass grit, metal fraction, ...).
Wastes containing mercury

Fig. 12.1 processing waste containing mercury – MRT System

The output of the recycling process is represented by these material components:
- mercury
- glass
- metal – aluminium, steel
- luminophore.

Processing in the Czech Republic

RECYKLACE EKOVUK a.s. is a company engaged in mercury waste recycling in the Czech Republic.

Recycling technology

Mechanical treatment (shredding) and sorting of waste separates the part contaminated with mercury and the directly usable components such as glass, non-ferrous metals, iron, etc.

The waste is disposed thermally in an electric rotary furnace at 600 °C. The present mercury and other volatile pollutants, including organic substances, which are found, e.g. in putties, kartit, etc., are converted into gaseous form and removed from the waste. Dust particles are separated from thermal process gases, and organic substances are decomposed and burnt by means of oxidation at high temperatures. Mercury is obtained by cooling the vapours, any remaining mercury is captured on adsorbers. This mercury is used as a secondary raw material.

12.4 Toxicity of mercury

Mercury belongs among elements, the effect of which on the human organism health is unambiguously negative. It is a cumulative poison, excreting from the organism only very slowly. Toxicity is influenced by the form of mercury and exposure duration – elemental mercury is often excreted without any effect to the organism. Mercury vapours after inhalation are quickly absorbed by the blood circulation and transported to the target organ – brain, where mercury is deposited.

Inorganic compounds are toxic, whereas mercurous compounds are less toxic than mercuric ones. Organic mercury compounds cause damage in brain and nervous system. Methylmercury is the most dangerous mercury compound. This can originate from inorganic compounds through methanogenic bacteria in the anaerobic environment especially in sediments of fresh as well as salt waters. Liquid methylmercury or dimethylmercury originates through this process. Methylmercury belongs among embryotoxic and mutagenic substances.
Wastes containing mercury

∑ Sumary of terms

At the end of the chapter are repeated the main terms that you should acquire:

Wastes containing mercury

Hazardous waste

❓ Question to the topic

1. Which waste may contain mercury?
2. What are the procedures for mercury removing from waste?
3. What are the technologies for processing waste of fluorescent lamps?

📖 References


metals and their alloys).


13. Wastes containing tungsten

**Study time:** 3 hours

**Objective** After reading this paragraph, you will be able to

- define tungsten wastes
- describe the technologies of tungsten waste processing
- describe the recycling technologies of tungsten carbide scrap

**Lecture**

13.1 Tungsten and its alloys

Tungsten is a very weight and extremely difficult to melt metal. It has the highest melting point of all metals and highest density of base metals. In the pure state is tough. At room temperature, tungsten is very stable and corrosive resistant. Tungsten is a refractory metal.

**Properties:**

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Symbol</td>
<td>W (Wolframium)</td>
</tr>
<tr>
<td>Atomic weight</td>
<td>183.85 g·mol⁻¹</td>
</tr>
<tr>
<td>Density</td>
<td>19.25 g·cm⁻³</td>
</tr>
<tr>
<td>Melting point</td>
<td>3 422 °C</td>
</tr>
<tr>
<td>Boiling point</td>
<td>5 555 °C</td>
</tr>
</tbody>
</table>

**Application:**

Tungsten is a component of various alloys, particularly steel. It is also a component of nickel ("Hastelloy C-276" - 4% W) and cobalt alloys ("Stellite 1" - 13 % W) with content 0-15 % W. In pure form, it is used for the manufacture of bulb filaments. It is used in electrical engineering as a material for vacuum tube anode. Tungsten electrodes are used for tungsten inert gas welding of metals (TIG).

Tungsten alloys are used for metal-working tools, drilling heads of geological tools, turbines and other highly thermally and mechanically stressed components, special cutting tools, and dental application tools. Tungsten heavy alloys (WHA) are produced by powder metallurgy focused on the desired properties of the final product. Due to its high density, it is used as the material for penetration projectiles (penetrators).

A very important area of use is represented by cutting tools made of cemented tungsten carbides for CNC machining = cemented carbides = hardmetals. They are produced by powder metallurgy. They consist of fine particles of hard carbides of some metals, such as W, Ti and Ta, which are bonded with each other, usually by cobalt.

13.2 Tungsten wastes

Waste tungsten and its alloys are quite common. They are frequently found in worn tools from steels with higher tungsten content. Valuable sources of secondary tungsten include worn cutting tools made of cemented carbides based on tungsten. Pure tungsten is found in the form of bulb filaments.
Tungsten wastes

The most commonly processed W wastes are:

• pure tungsten - tungsten filaments, various components, …
• tungsten alloys – eg. tool steel (drills), …
• cemented carbides - cutting tools (lamella, drill head, ...), ….

According to the standards, waste tungsten and tungsten alloys have the class designation of 941

13. 3 Processes used for the treatment of tungsten waste

Recycling of tungsten is carried out only in the USA, Japan and Western Europe. They are mostly worn tool tips from cemented carbides.

The following types of wastes are most commonly processes:

• **cemented carbide scrap** – acid leaching, zinc treatment, remelting, …
• **waste alloys**
  - in the form of chips, powders – air oxidation at the temperature of 800 °C, grinding, followed by a reduction using hydrogen at the temperature of 900-1000 °C – the product is W
  - in the form of components, discard heads, remains after forming (hard scrap) or powders, sludge, shavings (soft scrap) *- electrolysis (W waste is connected as an anode), acid leaching, leaching and milling (leach- milling), leaching in ferric chloride solution, remelting, reworking into ferrotungsten, …
• **milling and grinding bodies (mill products)** – alloying agents to superalloys (Ni, Co), steel, source of W for the production of cemented carbides, it can be reworked by means of the above-presented methods*
• **remains**
• **used catalysts**
• **steels and special alloys** - remelting during the production of steel (alloying)
• **tungsten electrodes** – it can be reworked by means of the above-presented methods*.

่า Cemented carbide wastes – main source of secondary W

Waste cemented carbide, or hardmetal waste, means waste cemented carbide containing tungsten, cobalt, titanium, tantalum, and niobium. Although the main component is usually tungsten, other elements such as cobalt and tantalum have several times higher price.

The technologies used for the recycling waste cemented carbide can be divided into:

• direct with a physical nature (“Zn-treatment process” - pyrometallurgical processing)
• indirect, based on the oxidation and subsequent chemical processing of the oxidation products (processing using the wet method – leaching, hydrometallurgical processing),
• specific processes (“Coldstream process”,…).

1. Indirect alkaline process:
• the input material is first subjected to oxidation and subsequently leached in an alkaline environment,
• the solution is then subjected to extraction and conversion into an intermediate product of ammonium tungstate that is further processed.

2. HMZ process:
• the technology is based on the oxidation calcination of wastes in a rotary retort furnace,
• the calcined scrap is leached in a sulphuric acid solution with the separation of cobalt and other soluble components, where heptahydrate cobalt sulphate is the product from the liquid phase after the separation on a filter,
• solid phase, the acidic insoluble leaching residue, is leached in a solution of ammonia,
Tungsten wastes

- and the evaporation and crystallisation of the leach forms crystalline ammonium paratungstate for the reduction and manufacturing of powdered tungsten,
- the filtering residue (acidic insoluble leaching residue) contains the rest of tungsten, Ta and Nb as a valuable raw material is sold to foreign processors.

3. Zinc treatment:
- worn cutting tools from cemented carbides are mixed with lump pure zinc and the mixture is heated in a furnace (Fig. 13.1),
- liquefied zinc penetrates through the carbide plates, it disrupts them and transforms them into sponge,
- the material is easy to grind and the obtained powder can be used for the original purpose.

[Zn: Zinc  Co: Cobalt  WC: Tungsten carbide]


Fig. 13.1 Zinc treatment

4. Wet-chemical treatment (Fig. 13.2):
- chemical processing using the wet method – waste is immersed in nitrate of soda and placed in a furnace where the mixture is heated,
- chemical reactions take place - melting,
- molten carbide is passed through a column – the ion exchange process,
- the product is WO₃ oxide.


Fig. 13.2 Wet-chemical treatment
5. Coldstream process:

- The sorted and cleaned hardmetal pieces are cooled then blasted onto a hard surface using high velocity streams of cooled air in a closed system (Fig. 13.3).

Fig. 13.3 Schema of Coldstream process (LASSNER, E., SCHUBERT, W. D. Tungsten. Properties, Chemistry, Technology of the Element, Alloys, and Chemical Compounds)

13.4 Toxicity of tungsten and its compounds

Metallic tungsten is not toxic. Tungsten is not a biogenic element, nevertheless, it can substitute molybdenum in some biogenic processes (creation of enzymes) thanks to their similarity. Workers in production of tungsten carbide may be exposed, affecting of respiratory tract may occur (coughing, reduced efficiency of the respiratory system, pulmonary inflammation diseases), then a weight loss and eventually death. A synergetic effect of cobalt is investigated, because tungsten carbides may increase solubility of highly toxic cobalt in body fluids.

Tungsten trioxide WO₃ is harmful to health at ingestion, irritates skin and may cause serious eye irritation. It is used as a pigment for dyeing of ceramics (green colour), plasma spraying (W coating).

∑ Sumary of terms

At the end of the chapter are repeated the main terms that you should acquire:
Tungsten wastes

Hardmetals scrap, cemented carbide scrap

Recycling of cemented carbide scrap

Question to the topic

1. What are tungsten wastes?
2. What are the technologies for processing tungsten waste?
3. What are the technologies for processing hardmetal scrap?

References


14. Heavy metals, IPPC

Study time: 2 hours

Objective After reading this paragraph, you will be able to
- define the basic terms of heavy metals
- define the basic terms of integrated prevention – IPPC, BAT, BREF
- describe and characterize the heavy metals based pollution sources

Lecture

14.1 Heavy metals

Along with technological development the production and consumption of non-ferrous metals, which were produced in incomparably less amounts - such as beryllium, titanium, germanium, gallium, vanadium, selenium, molybdenum, tungsten - has increased dramatically. The production and application of classic non-ferrous metals and their alloys - such as aluminum, lead, copper, nickel, chromium, antimony, mercury, … - has increased noticeably. An increase in concentration of these metals in the living environment increases, which is a serious problem!

Metals do not undergo chemical degradation and accumulate in underground soil layers. 

Soil microorganisms and aqueous microflora cause that a part of toxic metals enter the bond with organic substances, by which in many cases their toxicity multiplies or significantly changes!!! - e.g. alkylated mercury and arsenic. Elements undergoing biomethylation (alkylation) in the natural environment are Nickel (Ni), Tin (Sn), Antimony (Sb), Mercury (Hg), Lead (Pb), Arsenic (As), Selenium (Se), Germanium (Ge)… Toxic metals transfer to the human food chain!

However, plenty of metals are essential for the organism in trace concentrations - such as Cr, Cu, Zn or Fe, which are a part of some enzymes. Their deficiency may develop in a serious disease.

About 80 elements in the periodic table of the elements belong to metals, 30 of them are called toxic metals.

Trace metals - metals occurring in organisms or in the living environment in very low concentrations corresponding to only few ppm.

Heavy metals - metals the density of which is higher than 5 g·cm⁻³ (e.g. Cd, Hg, Pb).

Toxic metals - metals, which in specific concentrations have harmful effects on humans and other biotic ecosystem components.

Within “toxicology” the term “heavy metals” also covers other metals and metalloids (half-metals), such as arsenic, which have toxic effects.

Along with development of new knowledge on negative effects of particular metals and with regard to the actual occurrence of metals in new types of wastes, characteristics complementing a term ‘heavy metals’ have been defined step by step.
Heavy metals, their impact on humans and the environment

Heavy metals:
- Heavy or toxic metals are typically meant selected metals, the negative effect of which on animal and plant organisms has been proven.
- Heavy metals also include some elements from the transition area and some non-metals (As, B, Se).
- Radioactive metals are not categorized as heavy metals; their evaluation is performed with regard to another type of toxic effect preferentially determined by the emitted radiation effect.

Using available groundwork on toxicity of particular metals, the following classification is proposed according to a rate of their unwholesomeness:

I. HIGHLY HAZARDOUS METALS - Cd, Hg, Pb
II. MEDIUM HAZARDOUS METALS - Ag, Al, As, Be, Cu, Co, Cr, Ni, V, Zn
III. LOW HAZARDOUS METALS - Ba, Fe, Ga, Ge, Mo, Mn, Sb, Sn, Ti, W

Plenty of heavy metals are considerably toxic for humans, animals and plants, their dangerousness is increased by a summation effect – they are stored and accumulated in the organism through the food chain.
Some of them are carcinogenic, others mutagenic or teratogenic.
Hg, Pb, Cd, Cu, Zn exhibit a high accumulation coefficient.
Toxicity of heavy metals relate to their passability through cell membranes, their capability to bind to proteins and thus their ability to accumulate in some tissues.
Many metals block the activity of enzymes with -SH groups, thus influencing vital functions.

If intoxication by more metals at the same time occurs, their simultaneous effect may be influenced:
- amplification of effects = synergetic acting (e.g. Cd + Zn, Ni + Zn, Hg + Cu),
- attenuation of effects = antagonistic acting (e.g. Zn in a form of salts reduces the carcinogenic effect of cadmium, metals reduce the carcinogenic effect of benzo(a)pyrene).

Why are metals a hazardous group for health of organisms and need to be monitored in the environment?
1) Toxicity – often in very low concentrations (e.g. LD$_{50}$ As$_2$O$_3$ for humans 200 - 300 mg)
2) Bioaccumulation in the organism
3) Carcinogenity (Cd, As, Cr$^{VI}$, Ni, Be)
4) Nondegradability (indecomposableness), Persistence (stability)
5) Increase in concentrations in the environment (mainly in last 100 years).

Toxicity of substances

Toxicology is a science of adverse effects of substances on a living organism.
Toxicity reflects the degree of toxicity of the substance to the target organism or tissue.

Toxicity of substances depends on:
- a chemical structure
- a route of entry into the organism
- receptivity (sensitivity) of a target organism
- a time period of acting (exposure)
- a daytime of acting
- a physical condition, sex, age, weight of an individual etc.

Toxicity of a specific compound is determined by its structure, solubility in water and in acidic environment (stomach), which means absorbability in the organism. This depends on a way of
exposure (entry gate) – “which way and how a substance gets to the organism” (ingestion, inhalation, skin absorption …).

- **Ecotoxicology**

This is a boundary field between toxicology and ecology, dealing with effects of foreign substances on freely living organisms in their environment (environmental toxicology).

In a broad sense, this involves a transfer of pollutants from the environment to a human directly from environment components (water, air, soil) or indirectly through natural or human-directed food chains (food production).

- **Anthropogenic ways of entry of metals to the environment**

The most frequent anthropogenic ways of entry of metals to the environment (through human activity):

- mining
- metallurgy
- waste waters (+ runoff)
- textile industry
- production of dyes and plastics
- vehicles and automotive industry
- agricultural industry (Cd, fertilizers, pesticides …)
- fossil fuel burning (As, Cd, …)
- waste incineration, etc.

14. 2. IPPC – Integrated Pollution Prevention and Control

The process of the integrated pollution prevention and control is a process, the aim of which is to improve the living environment quality and to achieve a higher level of the environment protection in general.

The Integrated Pollution Prevention and Control – IPPC – process was implemented in the legal order of the Czech Republic on January 1, 2003, when the Act no. 76/2002 Coll. on integrated pollution prevention and control, on the integrated pollution register and on amendment to some laws (the Act on integrated prevention) came into force. On March 19, 2013, Act no. 69/2013 Coll. was published in the Collection of Laws; this act amended the Act no. 76/2002 Coll. on integrated pollution prevention and control, on the integrated pollution register and on amendment to some laws (the Act on integrated prevention), subsequently amended, and some other laws. The act came into force on the day of promulgation.

A principle of the integrated prevention is minimization of negative impacts of industrial and agricultural activities on the environment, the control of origination and transfer of pollution and a support of environmental approaches in industrial and agricultural plants.

This covers information on the Best Available Techniques (BAT), BREF reference documents and the Integrated Pollution Register of the environment.

- **Best Available Techniques - BAT**

The technical level of equipment, above all as to the achieved level of emissions and amount of wastes, material and energy demandingness and environmental management methods and tools, is compared to the **Best Available Techniques - BAT**.

BAT are the most effective and most advanced stages of development of activities and their operational methods, determining applicability of a certain technique as a base for determination of emission limits to prevent or at least reduce emissions and negative impacts on the complex living environment, while maintaining technical and economic availability. Thus, this is a comparison of
parameters of techniques and procedures using predetermined indicators (e.g. a specific emission to the living environment or the energy consumption per production unit). Through application of BAT as the pollution prevention a higher environmental protection level can be achieved.

With regard to the continuous development of techniques, the BAT standards, determined as a result of negotiations between the public and private sector, have been continuously moved. The system of information exchange on the best available techniques serves as a base for these negotiations, data processing and information intermediation.

The “Information Exchange Agreement” was concluded between resorts and subjects responsible for exchange of information on BAT. The Ministry of Industry and Trade, the Ministry of the Environment, the Ministry of Agriculture, CENIA (the Czech Environmental Information Agency) and the Czech Environmental Inspection are participants in this agreement.

A new information web www.ippc.cz was put into service for this purpose. The method and scope of organization of the system for the exchange of information on best available techniques is set in the Decree of the Government no. 63/2003 Coll. BREF reference documents are the result of the process of the exchange of information on best available techniques.

Referenční dokumenty – BREF

The results of the negotiations and the exchange of information on best available techniques are summarized in the so-called reference documents on the best available techniques (BREF documents) for particular categories of facilities.

The BREF reference documents review information on the European best available techniques. BREF are elaborated for particular industrial branches and cover data on industrial processes, used technologies, emission limits applied in EU member countries, priority material flows and monitoring.

BREF provides information on the technological level achieved within the given branch. The presented information is neither legally binding nor enforceable, however, this is a standard for decisions, whether a respective technology and operating method meet the requirements of IPPC act and whether a permit to operate the industrial facility will be issued.

A base of each BREF document is a description of BAT and information on the future BATs. For the BREF documents overview see „http://www.ippc.cz/obsah/referencni-dokumenty/“.

The very BREF documents are divided to BREF sectoral documents and BREF cross-sectoral documents.

Register of the environment

This is a publicly accessible information system of the public administration of the Czech Republic under the competent authority of the Ministry of the Environment and operated by CENIA, the Czech Environmental Information Agency.

IPR provides information on emissions to air, water and soil and on transfers of 93 reported substances, which are reported to the register directly by the environment polluters based on meeting the defined criteria.

IPR is one part of the Shared Environmental Information System (SEIS). The list and information on substances reported to the IRP are available at http://www.irz.cz/node/20.

Summary of terms

At the end of the chapter are repeated the main terms that you should acquire:

Heavy metals

Integrated Pollution Prevention and Control IPPC
Best Available Techniques BAT

BREF documents

The environmental pollution registers

Question to the topic

1. Explain the term of heavy metals within toxicology.
2. Which metals rank among heavy metals? Characterize their impact on the environment and humans.
3. What are the anthropogenic inputs of metals on the environment?
4. What are the goals and principles of the IPPC?
5. What is BAT?
6. What contain documents BREF?
7. What is the basic meaning of environmental pollution registers?

References

### Annexes

#### Annex no. 1  Annex III of Directive 2008/98 / EC - List of hazardous waste properties (properties of waste which render it hazardous)

<table>
<thead>
<tr>
<th>Code</th>
<th>Hazardous waste property</th>
</tr>
</thead>
<tbody>
<tr>
<td>HP1</td>
<td>Explosive</td>
</tr>
<tr>
<td>HP2</td>
<td>Oxidising</td>
</tr>
<tr>
<td>HP3</td>
<td>Flammable</td>
</tr>
<tr>
<td>HP4</td>
<td>Irritant</td>
</tr>
<tr>
<td>HP5</td>
<td>Single Target Organ Toxicity (STOT)/ Aspiration</td>
</tr>
<tr>
<td>HP6</td>
<td>Acute toxicity</td>
</tr>
<tr>
<td>HP7</td>
<td>Carcinogenic</td>
</tr>
<tr>
<td>HP8</td>
<td>Corrosive (Wastes which on application can cause skin corrosion.)</td>
</tr>
<tr>
<td>HP9</td>
<td>Infectious</td>
</tr>
<tr>
<td>HP10</td>
<td>Toxic for reproduction</td>
</tr>
<tr>
<td>HP11</td>
<td>Mutagenic</td>
</tr>
<tr>
<td>HP12</td>
<td>Release of an acute toxic gas cat 1, 2 or 3 (Wastes which release acute toxic gases cat. 1, 2 or in contact with water or an acid.)</td>
</tr>
<tr>
<td>HP13</td>
<td>Sensitising</td>
</tr>
<tr>
<td>HP14</td>
<td>Ecotoxic</td>
</tr>
<tr>
<td>HP15</td>
<td>Yielding another substance (Waste capable of exhibiting a hazardous property listed above not directly displayed by the original waste.).</td>
</tr>
</tbody>
</table>


<table>
<thead>
<tr>
<th>Code</th>
<th>Recovery operation</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>Use principally as a fuel or other means to generate energy</td>
</tr>
<tr>
<td>R2</td>
<td>Solvent reclamation/regeneration</td>
</tr>
<tr>
<td>R3</td>
<td>Recycling/reclamation of organic substances which are not used as solvents (including composting and other biological transformation processes)</td>
</tr>
<tr>
<td>R4</td>
<td>Recycling/reclamation of metals and metal compounds</td>
</tr>
<tr>
<td>R5</td>
<td>Recycling/reclamation of other inorganic materials</td>
</tr>
<tr>
<td>R6</td>
<td>Regeneration of acids or bases</td>
</tr>
<tr>
<td>R7</td>
<td>Recovery of components used for pollution abatement</td>
</tr>
<tr>
<td>R8</td>
<td>Recovery of components from catalysts</td>
</tr>
<tr>
<td>R9</td>
<td>Oil re-refining or other reuses of oil</td>
</tr>
<tr>
<td>R10</td>
<td>Land treatment resulting in benefit to agriculture or ecological improvement</td>
</tr>
<tr>
<td>R11</td>
<td>Use of waste obtained from any of the operations numbered R 1 to R 10</td>
</tr>
<tr>
<td>R12</td>
<td>Exchange of waste for submission to any of the operations numbered R 1 to R 11</td>
</tr>
<tr>
<td>R13</td>
<td>Storage of waste pending any of the operations numbered R 1 to R 12 (excluding temporary storage, pending collection, on the site where the waste is produced)</td>
</tr>
</tbody>
</table>


<table>
<thead>
<tr>
<th>Code</th>
<th>Disposal operation</th>
</tr>
</thead>
<tbody>
<tr>
<td>D1</td>
<td>Deposit into or on to land (e.g. landfill, etc.)</td>
</tr>
<tr>
<td>D2</td>
<td>Land treatment (e.g. biodegradation of liquid or sludgy discards in soils, etc.)</td>
</tr>
<tr>
<td>D3</td>
<td>Deep injection (e.g. injection of pumpable discards into wells, salt domes or naturally occurring repositories, etc.)</td>
</tr>
<tr>
<td>D4</td>
<td>Surface impoundment (e.g. placement of liquid or sludgy discards into pits, ponds or lagoons, etc.)</td>
</tr>
<tr>
<td>D5</td>
<td>Specially engineered landfill (e.g. placement into lined discrete cells which are capped and isolated from one another and the environment, etc.)</td>
</tr>
<tr>
<td>D6</td>
<td>Release into a water body except seas/oceans</td>
</tr>
<tr>
<td>D7</td>
<td>Release to seas/oceans including sea-bed insertion</td>
</tr>
</tbody>
</table>
Annexes

D8  Biological treatment not specified elsewhere in this Annex which results in final compounds or mixtures which are discarded by means of any of the operations numbered D 1 to D 12

D9  Physico-chemical treatment not specified elsewhere in this Annex which results in final compounds or mixtures which are discarded by means of any of the operations numbered D 1 to D 12 (e.g. evaporation, drying, calcination, etc.)

D10  Incineration on land

D11  Incineration at sea

D12  Permanent storage (e.g. emplacement of containers in a mine, etc.)

D13  Blending or mixing prior to submission to any of the operations numbered D 1 to D 12

D14  Repackaging prior to submission to any of the operations numbered D 1 to D 13

D15  Storage pending any of the operations numbered D 1 to D 14 (excluding temporary storage, pending collection, on the site where the waste is produced).