

# GUIDELINES FOR ENVIRONMENTALLY SOUND MANAGEMENT OF USED LEAD BATTERIES IN THE MEDITERRANEAN



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# GUIDELINES FOR ENVIRONMENTALLY SOUND MANAGEMENT OF USED LEAD BATTERIES IN THE MEDITERRANEAN



UNEP



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## PREFACE

This technical guide is focused on the environmentally sound management (ESM) of lead batteries and its ultimate objective is to provide the Mediterranean countries with information in order to establish a proper management system to prevent human health and environmental hazard. It has been developed by UNEP/MAP MED POL Programme in collaboration with the Basel Convention Regional Centre in Bratislava in 2014, under the MedPartnership project<sup>1</sup> and in the framework of MAP Programme of Work 2014-2015.

The management of used lead batteries refers to the overall process of collection, transport, recovery and/or disposal of used lead batteries, including the supervision of such operations. The system of environmental sound management of used lead batteries can be successfully implemented only when legislative rules are effective and applicable, all or at least most of producers /importers of lead batteries are participating in the system, facilities for lead recycling are available in appropriate distance (best of all in the country or in a not-very-far distance in neighbouring countries), and effective state control to prevent human health

and environmental hazard together with enhanced law enforcement. This technical guide provides background information and data on sources and amounts of produced used lead batteries, an overview of available standards, technical specification and guidelines on the storage and treatment of batteries and accumulators as well as information on associated environmental and health aspects. It also describes the collection, transport and storage, treatment and recovery of used lead batteries, as well as their transboundary movement. Finally it explains potential sources of environmental contamination, and discusses economic aspects of environmentally sound management of used lead batteries.

This guide was reviewed by an expert meeting and endorsed by the MAP Focal Points meeting in 2015. It is published online in English and French as an effort to support the Mediterranean countries

in implementing the relevant priority actions of the National Action Plans adopted in the framework of Article 5 and 15 of the LBS Protocol of the Barcelona Convention and its Strategic Action Programme SAP-MED.

1. The Strategic Partnership for the Mediterranean Sea Large Marine Ecosystem (MedPartnership) is a collective effort of leading organizations (regional, international, nongovernmental, etc.) and countries sharing the Mediterranean Sea towards the protection of the marine and coastal environment of the Mediterranean. The MedPartnership is being led by United Nations Environment Programme (UNEP) Mediterranean Action Plan (MAP) and the World Bank and is financially supported by the Global Environment Facility (GEF), and other donors, including the European Union (EU) and all participating countries.

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## DEFINITIONS

**Battery** - any device that stores energy for later use; common use of the word, "battery", however, is limited to an electrochemical device that converts chemical energy into electricity, by use of a galvanic cell.

**Galvanic cell** - a device consisting of two electrodes (an anode and a cathode) and an electrolyte solution; batteries may consist of one or more galvanic cells.

**Lead battery** - the electrical accumulator in which the active material of the positive plates is made up of lead compounds and that of the negative plates is essentially lead, the electrolyte being a dilute sulphuric acid solution.

**Used lead battery** - the battery which is no longer capable of being recharged or cannot retain its charge properly, its lifetime reaches its end and it becomes a waste.

**Management of used lead batteries** - the overall process of collection, transport, recovery and or disposal of used lead batteries, including the supervision of such operations.

**Separate collection** - the gathering of used lead batteries, including the preliminary sorting and preliminary storage of used lead batteries for the purposes of transport to a treatment facility.

**Storage** - placing of used lead batteries in the room of waste management or treatment facilities in sites with impermeable surfaces and suitable weatherproof covering

or in suitable containers.

**Treatment of used lead batteries** - means recovery or disposal operations with used lead batteries, including preparation prior to recovery or disposal

**Recovery** - means any operation the principal result of which used lead batteries serving a useful purpose by replacing other materials which would otherwise have been used to fulfil a particular function, or waste being prepared to fulfil that function, in the plant or in the wider economy

**Recycling** - means any recovery operation by which used lead batteries materials are reprocessed into products, materials or substances whether for the original or other purposes

**Fractions of used lead batteries** - material parts and pieces produced from treatment of used lead batteries and relevant by-products of used lead batteries

**Disposal** - means any operation which is not recovery even where the operation has as a secondary consequence the reclamation of substances or energy.

## DESCRIPTION OF A LEAD BATTERY

A battery mainly consists of electrodes (two plates, made from lead) placed in an electrolyte solution (sulphuric acid). The metal in the anode oxidises releasing negatively charged electrons and positively charged metal ions. The electrons travel

from the anode to the cathode. The electrons combine with the material in the cathode through reduction and release a negatively charged metal – oxide ion. When the anode is fully oxidised or the cathode is fully reduced, the chemical reaction will stop and the battery is considered to be discharged. The schematic description of a lead battery is shown in Figure 1.

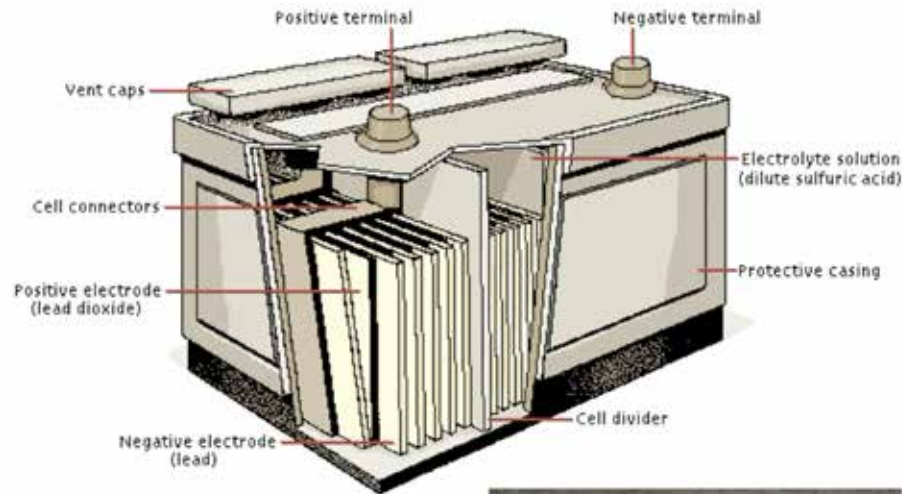


Fig. 1: Schemes of a lead battery and pictures with its labelling  
(Author: Neil McNiven)

**Positive and negative terminals:** made of lead, and where the external electricity consumer devices are connected;

**Plugs:** one for each battery element, where distilled/deionised water can be replaced whenever needed and also to provide an escape route for gases formed in the cells;

**Connectors:** made of lead, that makes electrical contact between plates of same polarity and also makes electrical contact between separated elements;

**Cap and box:** originally made of ebonite, but now more commonly made from either polypropylene or co-polymer; Sulphuric acid solution: the electrolyte of the battery;

**Element separators:** usually a part of the box and made of the same material provide chemical and electrical isolation between the electrical elements. They are connected in a serial layout in order to increase the final voltage of the battery;

**Plate separators:** made of PVC or other porous materials, avoid physical contact between two contiguous plates but, at the same time, allowing free movement of ions in the electrolyte solution;

**Negative plates:** constituted by a metallic lead grid covered by a lead dioxide (PbO<sub>2</sub>) paste;

**Positive plates:** constituted by metallic lead plates;

**Battery element:** a series of negative and positive plates placed consecutively and isolated between each other with plate

separators. Plates of same polarity are electrically connected.

The battery plates are constituted by metallic lead structures, known as grids, covered by a lead dioxide paste, in the case of the negative plates, or by a porous metallic lead paste, in the case of the positive plates. The lead used in both the plates may also contain several other chemical elements such as antimony, arsenic, bismuth, cadmium, copper, calcium, silver, tin and sometimes other elements. The plates manufacture process also uses expander materials, such as barium sulphate, lampblack and lignin added in order to prevent the plate retraction during use. Once prepared, the plates are dried, cured and shaped ready to be assembled into the battery elements.

Automotive battery manufactures produce a full range of starter batteries for all types of vehicles using petrol and diesel engines. The characteristic of lead acid batteries are large weight, relatively short shelf life without recharge, and a good ability to deliver high currents. Lead batteries are very adapted for uses requiring (occasional) high current draw, and where charging is regular (i.e. automotive). The lead battery has high energy storage capacity and low cost.

## ENVIRONMENTAL AND HEALTH ASPECTS

Used batteries pose a threat to our environment and should be managed properly. The toxic materials present in the battery can cause harm to the environment and to human beings also. This is the reason why waste battery recycling should be done properly. The incorrect management of waste lead batteries cause danger to waters, soil and air, as well as to human health. Batteries are safe, but precaution applies when touching damaged cells and when handling lead acid systems that have access to lead and sulphuric acid. Lead batteries are labelled as hazardous material.

Lead is a toxic metal that can enter the body by inhalation of lead dust or ingestion when touching the mouth with lead-contaminated hands. If leaked onto the ground, the acid and lead particulates contaminate the soil and become airborne when dry. Exposure to lead causes a variety of health effects, and affects children in particular. Lead is a metal with no known biological benefit to humans. Too much lead can damage various systems of the body including the nervous and reproductive systems and the kidneys, and it can cause high blood pressure and anaemia. There is no known safe blood lead concentration. But it is known that, as lead exposure increases, the range and severity of symptoms and effects also increases.<sup>3</sup>

The sulphuric acid in a lead acid battery is highly corrosive and is potentially more harmful than acids used in other battery systems. Eye contact can cause permanent blindness; swallowing damages internal organs that can lead to death.

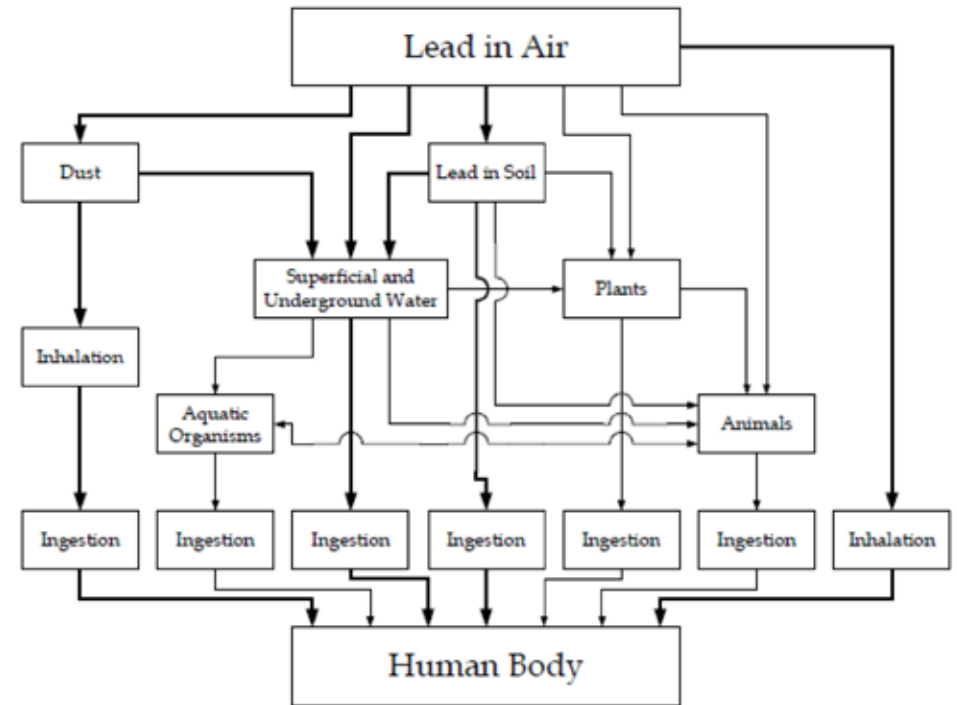


Fig. 2: Major pathways of human lead intake<sup>1</sup>

There are many facilities which have implemented scrap battery recycling as part of their pollution prevention efforts. The facility that makes the decision to implement used battery recycling will help to protect the environment and insure the compliance with environmental laws. There are many benefits of the lead battery scrap processing.

- Used battery recycling keeps all the hazardous metals in one place;
- The metals obtained in discharged car battery processing are reused in manufacturing process to build more batteries;
- The plastic (PP) from outer case of battery

is also recycled for further use;

- Lead waste battery processing follows good environmental policy;
- The battery scrap recycling saves natural resources.

The major use of lead in the world is in the form of lead acid batteries. Lead acid storage batteries are an essential component of the automotive industry for which there are currently no electro-chemical, economic or environmentally acceptable alternatives. So this makes the used battery recycling more important. Lead recycling saves money, lead and most importantly, the environment.



### SOURCES OF WASTE LEAD BATTERIES, ESTIMATION OF AMOUNTS OF PRODUCED USED LEAD BATTERIES

Lead batteries are used in vehicles of all types. As the amount of vehicles is gradually increasing all around the world, the amount of used batteries is also growing (in Figure 3, 4 and 5 the examples of the European market for automotive batteries are shown).

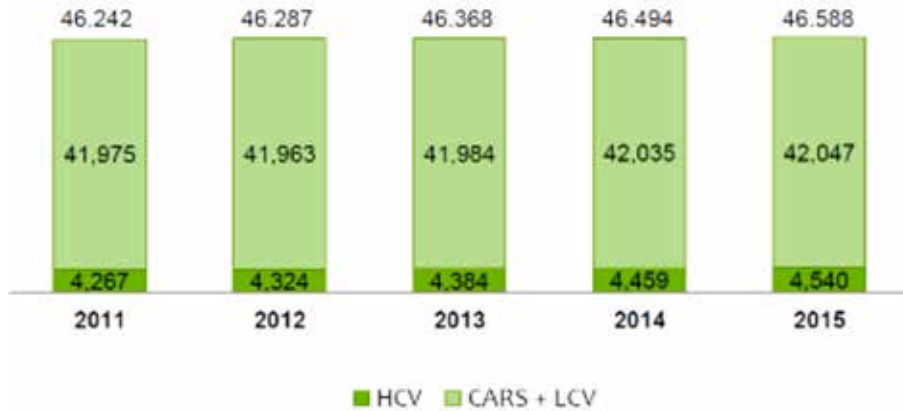


Fig. 3: Vehicle Production Europe and the outlook 2011-2015 (in k units) for CARS, HCV - Heavy Commercial Vehicles and LCV - Light Commercial Vehicles, Automotive Battery Committee, 2012

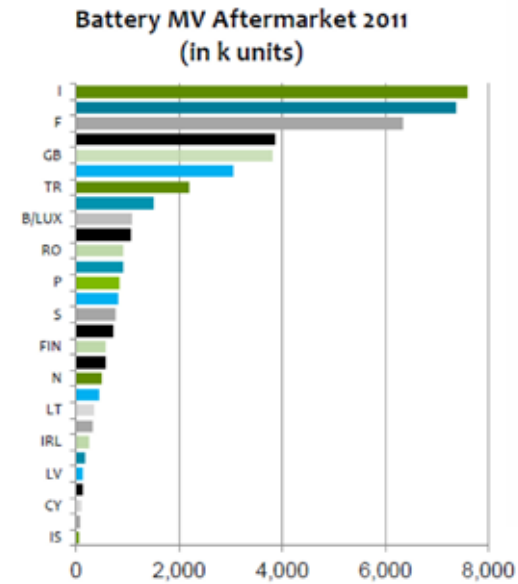


Fig. 4: Aftermarket battery volume for EU (2011 – 2015, in k Units).<sup>5</sup>

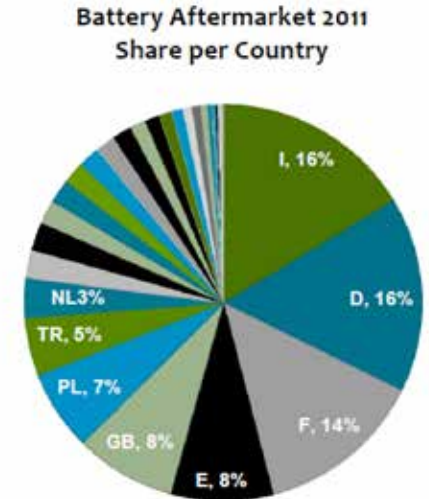


Fig. 5: Aftermarket battery per country in 2011.<sup>5</sup>

Another example is the consumption of lead acid batteries in Australia provided by the Australian Battery Recycling (ABRI) Initiative from 2010 [6]. In total, about 9.2 million lead acid batteries are purchased and 7.8 million reach the end of their useful life in Australia every year. By weight, lead acid batteries make up 91 %, or over 120,000 tonnes of the batteries disposed of in Australia. Australian

households purchase more than 7.6 million or 86,000 tonnes of lead acid batteries each year, and dispose of more than 6.4 million or 92,000 tonnes of them. Lead acid batteries are most commonly used in cars, according to both the Pollinate and the ABRI research (see Table 1). Car batteries make up 63 % of all lead acid batteries used in Australia.

Table 1: Lead acid battery use in Australian households reported by Australian Battery Recycling Initiative in 2010 based on the survey.<sup>6</sup>

%	Q1 Items owned	Q2 Most recent change
Car	87	80
Home alarm systems	23	12
Motorcycle	8	3
Boat	8	2
Solar panel	19	2
Electric scooter	1	1
None of these	11	-
n	1000	893

Q1: Which of the following items do you have?

Q2: Which of the following items had their battery changed MOST recently?

Base: Total sample Australians aged 14 – 64 (September 2011, n = 1000)

The source of used lead batteries in the country are mostly professional car services, construction companies using internal car maintenance, agricultural farms using internal car maintenance and some other

industrial companies. In countries with lower living standard also individuals change car batteries by themselves and households represent an important source of used lead batteries. In European countries the amount of produced used lead batteries per inhabitant and year is approximately 1.2 – 1.5 kg. A typical composition of lead – acid battery scrap is given in Table 2<sup>7</sup>.

Table 2: Composition of typical lead – acid automotive battery scrap<sup>7</sup>

Component	Wt - %
Lead (alloy) component (grid, poles...)	25 - 30
Electrolyte paste (fine particles of lead oxide and lead sulphate)	35 - 45
Sulphuric acid (10 – 20% H <sub>2</sub> SO <sub>4</sub> )	10 - 15
Polypropylene	4 - 8
Other plastics (PVC, PE, etc.)	2 - 7
Ebonite	1 - 3
Other materials (glass, etc.)	< 0.5

## OVERVIEW OF AVAILABLE STANDARDS, TECHNICAL SPECIFICATION AND GUIDELINES ON THE STORAGE AND TREATMENT OF BATTERIES AND ACCUMULATORS

### 5.1. European Union Legislative Framework

The European Commission's "Questions and answers on the Batteries Directive"<sup>8</sup> provide an introduction to the requirements which must be met by EU waste battery treatment systems and to the requirements which must be met during export of waste batteries:

- Does the EU Batteries Directive (2006/66/EC)<sup>9</sup> lay down any requirements for treatment of waste batteries?
  - In addition to levels of recycling efficiency, the Directive specifies how waste batteries are to be treated. The minimum requirement is that fluids and acids must be removed. The Directive also describes the conditions under which waste batteries must be treated and stored (Article 12(2) and Annex III, Part A).
- What requirements must be met if batteries are exported for recycling?
  - When waste batteries are exported outside the European Union, Member States must require sound evidence that the recycling takes place under conditions

equivalent to those set out in the EU Batteries Directive, including recycling efficiencies.

Article 12(2) and Annex III, Part A of the EU Batteries Directive (2006/66/EC)<sup>9</sup> set following requirements on waste battery treatment:

- Exclusively best available techniques are to be used.
- The minimum requirements set to be met include:
  1. Treatment shall, as a minimum, include removal of all fluids and acids.
  2. Treatment and any storage, including temporary storage, at treatment facilities shall take place in sites with impermeable surfaces and suitable weatherproof covering or in suitable containers.
- Recycling processes shall achieve the following minimum recycling efficiencies:
  - a) recycling of 65 % by average weight of lead-acid batteries and accumulators, including recycling of the lead content to the highest degree that is technically feasible while avoiding excessive costs;
  - b) recycling of 75 % by average weight of nickel-cadmium batteries and accumulators, including recycling of the cadmium content to the highest degree that is technically feasible while avoiding excessive costs; and
  - c) recycling of 50 % by average weight of other waste batteries and accumulators.

In Article 13 of the EU Batteries Directive (2006/66/EC)<sup>9</sup> it is recommended

- that Member States shall encourage the development of new recycling and treatment technologies and
- that Member States shall encourage treatment facilities to introduce certified environmental management schemes (e.g. EMAS or ISO 14000).

No further details on how to treat waste batteries and accumulators are provided by EU legislation<sup>9</sup>.

### **5.2. Best Available Techniques Reference Documents of the European Commission**

In order to specify what the Best Available Techniques for the respective sectors and industrial processes are a number of

Reference Documents on Best Available Techniques (BREFs) were prepared on the request of the European Commission. A dedicated BREF on waste battery treatment does not exist. However, following BREFs contain some specifications which are relevant for waste battery treatment:

- A) Reference Document on Best Available Techniques on Emissions from Storage<sup>10</sup> (for a summary of this BREF see Table 3).
- B) Reference Document on Best Available Techniques in the Non Ferrous Metals Industries,<sup>11,7</sup> (for a summary of this BREF see Table 4).
- C) Best Available Techniques (BAT) Reference Document for Iron and Steel Production,<sup>12</sup> (for a summary of this BREF see Table 5).

*Table 3: Summary of the BREF on Emissions from Storage<sup>10</sup>*

The BREF on Emissions from Storage addresses the storage and the transfer/handling of liquids, liquefied gases and solids, regardless of the sector or industry. It addresses emissions to air, soil and water. However, most attention is given to emissions to air. Energy and noise are also addressed but to a lesser extent.

Following storage methods for solids are addressed in particular:

- Heaps
- Sacks and bulk bags
- Silos and bunkers
- Packaged dangerous solids
- Containers and the storage of containers.

For the transfer and handling of solids, techniques such as mobile unloading devices, grabs, dump pits, fill pipes, thrower belts, conveyors and feeders are described. In each case the emission sources are identified.

*Table 4: Summary of the BREF on Best Available Techniques in the Non Ferrous Metals Industries<sup>7,11</sup>*

The BREF on best available techniques in the Non Ferrous Metals Industries covers the techniques for the production of both primary and secondary non-ferrous metals. The production of 42 non-ferrous metals and the production of ferro alloys are addressed. Ten groups of metals with similar production methods are dealt with in the document:

- Copper and its alloys, Tin and Beryllium
- Aluminium and its alloys
- Zinc, Lead, Cadmium, Antimony and Bismuth etc.
- Precious metals
- Mercury
- Refractory metals, e.g. Chromium, Tungsten, Vanadium, Tantalum, Niobium, Rhenium, Molybdenum
- Ferro alloys, e.g. IronChromium, IronSilicon, IronManganese, SiliconManganese, IronTitanium, IronMolybdenum, IronVanadium, IronBoron
- Alkali and alkaline earth metals, Sodium, Potassium, Lithium, Strontium, Calcium, Magnesium and Titanium
- Nickel and Cobalt
- Carbon and graphite electrodes. The production of carbon and graphite anodes is included because of the production of anodes at some aluminium smelters as an integral part of the production process.

*Table 5: Summary of the Best Available Techniques (BAT) Reference Document for Iron and Steel Production<sup>12</sup>*

The BREF on Best Available Techniques for Iron and Steel Production covers the processes involved in the production of iron and steel in integrated works as well as the production of steel in electric arc furnace steelworks. The main operations covered are:

- Loading, unloading and handling of bulk raw materials
- Blending and mixing of raw materials
- Coke production
- Sintering and palletisation of iron ore
- Production of molten iron by a blast furnace route, including slag processing
- Production and refining of steel using the basic oxygen process, including upstream ladle de-sulphurisation, downstream ladle metallurgy and slag processing
- Production of steel by electric arc furnaces, including downstream ladle metallurgy and slag processing
- Continuous casting.

Other downstream metal processing activities can be found in other BREF documents (e.g. see BREF on Ferrous Metals Processing Industry [12] or BREF on Smitheries and Foundries Industry<sup>14</sup>)

D) Reference Document on Best Available Techniques for the Waste Treatment Industries<sup>13</sup> (for a summary of this BREF see Table 6).

*Table 6: Summary of the BREF for the Waste Treatment Industries<sup>13</sup>*

The BREF for the Waste Treatment Industries covers the installations of a number of waste (hazardous and non-hazardous) treatment processes, and deals with:

- Common waste treatment processes such as temporary waste storage, blending and hou, repackaging, waste reception, sampling, checking and analysis, waste transfer and handling installations, and waste transfer stations
- Biological waste treatment processes such as aerobic/anaerobic treatment processes and mechanical and biological treatment processes
- Physico-chemical waste treatment processes of such as neutralisation, chromic acid and cyanide treatment, dewatering, filtration, harbour reception facilities, oil/water separation, precipitation, separation of Mercury from waste, settlement, solidification and stabilisation, and UV and ozone treatment
- Treatment processes to recover waste material for secondary use such as the re-concentration of acids and bases, the recovery of metals from liquid and solid photographic waste, the regeneration of organic solvents and spent ion exchange resins, and the re-refining of waste oils
- Treatment processes to produce mainly solid and liquid fuels from hazardous and non-hazardous waste.

The Best Available Techniques from the BREF for the Waste Treatment Industries<sup>13</sup> are of special importance for meeting the requirements set out in Annex III Part A of the EU Batteries Directive<sup>9</sup>. Some examples on relevant topics from this BREF are:

- Requirements for the treatment of waste containing mercury;
- Requirements to be considered during

- crushing, shredding and sieving operations;
- Best Available Techniques to prevent or control emissions;
  - Best Available Techniques to prevent soil contamination;
  - Best Available Techniques for storage and handling;
  - Best Available Techniques on the management of the residues generated by the waste treatment process.

### **5.3. Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and Their Disposal**

Basel Convention on the Control of Transboundary Movements of the Hazardous Wastes and Their Disposal regulates conditions for transboundary shipment of hazardous wastes to protect environment of the developing countries from the negative effects of inappropriate waste disposal. The Secretariat of the Basel Convention has published several guidelines, one of them dealing with management of waste lead – acid batteries<sup>1</sup>. The guideline in detail describes applied technologies of waste lead batteries treatment and recycling together with environmental and health aspects.

### **5.4. Guidelines on best available techniques and provisional guidance on best environmental practices of the Stockholm Convention**

The **Guidelines on best available techniques and guidance on best environmental practices** is the harmonized framework and guidance initiated by UNEP Chemicals which provide the necessary guidance called for in paragraph c) of the Article 5 of the Stockholm Convention. The use of best available techniques and the promotion of the application of best environmental practices shall be promoted in some cases and required to minimize releases of POPs

from unintentional production<sup>24</sup>. Thermal process of used lead batteries in the metallurgical industry i.e. secondary lead smelting involves the production of lead and lead alloys, primarily from scrap automobile batteries, and also from other used lead sources (pipe, solder, drosses, lead sheathing). Production lead processes include lead batteries scrap treatment, smelting and refining. Incomplete combustion; high levels of oils, plastics and other organic materials in feed; and temperatures between 250°C and 500°C may all give rise to chemicals listed in Annex C of the Stockholm Convention. Polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) performance levels associated with best available techniques for secondary lead smelters are <0.1 ng I-TEQ/Nm<sup>3</sup> (at operating oxygen concentrations). Best available techniques include the use of plastic-free and oil-free feed material, high furnace temperatures above 850°C, effective gas collection, afterburners and rapid quench, activated carbon adsorption, and dedusting fabric filters.

### **General information on emissions from secondary lead smelters**

Air emissions from secondary lead smelting can escape as stack or fugitive emissions, depending on the facility age or technology. Main contaminants are sulphur dioxide (SO<sub>2</sub>), other sulphur compounds and

acid mists, nitrogen oxides (NO<sub>x</sub>), metals (especially lead) and their compounds, dusts and traces of PCDD and PCDF. SO<sub>2</sub> is collected and processed into sulphuric acid in acid plants. Fugitive SO<sub>2</sub> emissions can be controlled by good extraction and sealing of furnaces. NO<sub>x</sub> can be reduced using low-NO<sub>x</sub> or oxy-fuel burners. Particulate matter is collected using high-efficiency dust removal methods such as fabric filters and returned to the process.

#### Emissions of PCDD/PCDF to air during the smelting process

The most problematic PCDD/PCDF are formed during base metals smelting through reaction of products of incomplete combustion, unburnt organic contaminants and chlorine compounds, usually by de novo synthesis in the cooling zone at temperatures between 250°C and 450°C. PCDD/PCDF or their precursors may be present in some raw materials and there is a possibility of de novo synthesis in furnaces or abatement systems. PCDD/PCDF are easily adsorbed onto solid matter and may be collected by all environmental media as dust, scrubber solids and filter dust. The presence of oils and other organic materials on scrap or other sources of carbon (partially burnt fuels and reductants, such as coke), can produce fine carbon particles which react with inorganic chlorides or organically bound chlorine in the temperature range of 250°C to 500°C to produce PCDD/PCDF.

Although PCDD/PCDF are destroyed at high temperature (above 850°C) in the presence of oxygen, the process of de novo synthesis is still possible as the gases are cooled through the 'reformation window' [24]. Full description of primary and secondary measures on PCDD/PCDF minimization is given in the chapter «Thermal processes in the metallurgical industry not mentioned in Annex C, part II» of the «Guidelines on BATs and Provisional Guidance on BEPs» of the Stockholm Convention.

## COLLECTION, TRANSPORT AND STORAGE OF USED LEAD BATTERIES

The used lead batteries are an important source of environmental hazard and it is necessary to operate the effective system of management of used lead batteries. The result of the system is the environmentally safe handling and disposal of lead wastes as well as the production of valuable secondary raw materials.

The life cycle of lead batteries consists of these steps:

1. Production
2. Consumption
3. Collection and sorting
4. Transport
5. Storage
6. Treatment (dismantling)

7. Recovery (recycling)
8. Disposal

The scheme of life cycle of lead batteries is shown in Figure 6.

The used lead batteries system consists of the steps 3 to 8. All these activities must be under the strict control of authorities including the permit system for waste management activities.

There are listed the most comprehensive ways of treatment and requirements identified by an investigation of many potential sources:

General treatment of lead accumulators

- Collected waste batteries and accumulators shall be stored in weatherproof conditions in leak proof containers that are acid-resistant.
- Lead accumulators shall be treated

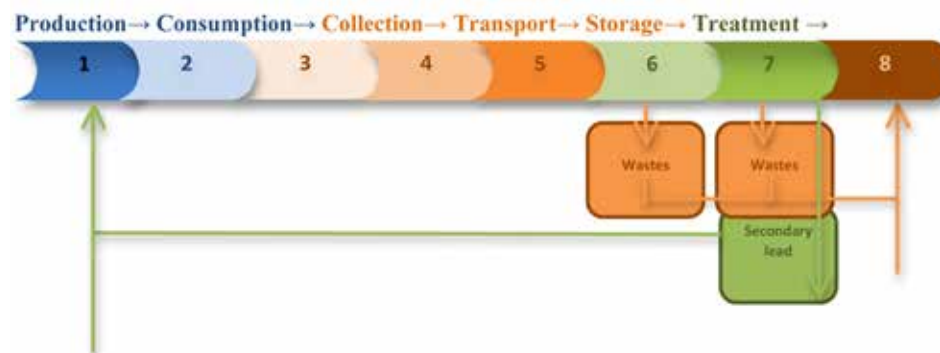


Fig. 6: Scheme of the life cycle of lead batteries

separately from all other batteries and accumulators.

- At any rate, the treatment of lead accumulators shall demonstrably recover lead and plastics of adequate purity so that they can be recycled and thus, shall ensure their re-introduction in the production cycle.
- The treatment shall include measures to prevent diffusive lead emissions.
- Free sulphuric acid shall be recovered.

### **6.1. General occupational health and safety recommendations for workers during the waste management and treatment of used lead batteries**

The actions and certain recommended measures in connection with occupational health and safety should be taken to improve waste management and treatment of used lead batteries of each treatment plant, and to achieve good environmental control practices.

From the health point of view, the proposed preventive measures are activities that should be observed in the occupational environment in order to prevent the workers exposed to lead from suffering adverse effects of lead contamination.

First aid treatment that is necessary part of each facility in case of contact with sulphuric acid calls for flushing the skin for 10 to 15 minutes with large amounts of water to cool the affected tissues and to prevent secondary damage. Immediately remove contaminated clothing, thoroughly wash the

underlying skin and call for the doctor.

The most important proposed measures are to:

- (a) consider every material containing lead as a possible source of environmental and human contamination;
- (b) keep the work environment in compliance with the national regulations for industrial safety;
- (c) segregate the work and eating areas i.e. prohibit eating and smoking inside the working areas;
- (d) prohibit children and pregnant women from working in lead recycling facilities;
- (e) undertake the development of educational and informative programs;
- (f) ensure the use of personal protection equipment in working places containing at least:
  - effectively protective cloth;
  - hard hats and safety footwear;
  - daily clean-up of the used cloths;
  - check and clean respirators daily;
  - protective masks which may vary in accordance of the average lead concentration in air;
- (g) control the lead concentrations in the working environment;
- (h) demand periodic medical checks of lead exposed workers;
- (i) enforce showering at the end of work.

### **6.2. Collection and sorting of used lead batteries**

As used batteries are a valuable source of lead it is important to provide separate

collection under controlled conditions to get the material for recovery as clean as possible. The second reason for controlled collection is environmental protection to prevent unprofessional dismantling with release of electrolyte to waters or soil.

The aim of separate collection is to get the used lead batteries from waste producers to authorised treatment facilities to prevent environmental and health hazards. The outcome of the project<sup>2</sup> proposed the extended producer responsibility where the producers (importers) are obliged to provide (prepare, organise and finance) the system of waste collection, treatment and disposal. The producers will provide one or several systems of

separate collection of waste batteries in order to meet collection limits given by legislation. There are several systems of separate collection of used lead batteries. The simplest system is collection at sources, in vehicle services where the important amounts of used lead batteries are arisen. The services have special containers for used lead batteries. It is prohibited to open or dismantle waste batteries. The container should be double-bottomed and market with notice containing information on the waste type, hazardous properties and first-aid instructions. The batteries should be placed into the container bottom down to prevent spilling of the electrolyte.



Fig. 7: Container for separate collection of used lead batteries in vehicle service



Fig. 8: Container for separate collection of used lead batteries in gas station in Slovakia

The other separate collection system is the collection in gas stations. Gas station is equipped with double-bottom container where the used lead batteries are placed (bottom down). Take-back system in specialised shops can be also introduced; the seller (distributor) of new lead batteries could be obliged to take back waste battery when the customer is buying a new one. It is required that the system is legally set in the country which decides the environmentally sound management of used lead batteries.

The next system is mobile collection organised by producers in cooperation with municipalities. The vehicle responsible for shipment of hazardous wastes having all permits and marking collects used lead batteries in municipalities in given term and given place. This system enables to collect used batteries from households and small facilities as farms or small services. The used lead batteries can be also collected in collection points operated by municipalities in special containers.



Fig. 9: Collection point operated by municipality Košice (Slovakia)

All collection systems are organised and financed by producers (importers). It is expected that collection is realised on the basis of agreements between operators of collection places (gas stations, services, municipalities) and producers (importers). It is acceptable to realise the separate collection on the basis of the agreement between operator of collection place and authorised treatment facility. It is necessary to control that all collected waste batteries will get to the authorised treatment facility or exported in accordance with the Basel Convention. Based on the different treatment requirements and treatment options for

the different battery types, a classification of batteries and accumulators according to different battery chemistry types, like the one shown in Table 7, is recommended. Batteries and accumulators should be sorted and prepared for separate treatment according to these battery chemistry types. Due to the different characteristics of batteries containing liquids and other batteries, a differentiation between batteries containing liquids and batteries which are free of liquids is proposed (see also different recommendations for storage – chapter 6.4). A mixture of liquid and non-liquid containing waste batteries should be regarded as batteries containing liquids.

Table 7: Recommended sorting fractions of batteries and accumulators

Sorting fraction - Battery type according to battery chemistry	Remarks
Pb-acid accumulators - liquid	including sealed lead acid accumulators with non-fixed electrolyte (using a catalyst to re-combine hydrogen and oxygen)
Pb accumulators – others	in sealed accumulators (sealed lead accumulators - SLA) the electrolyte is fixed by adding silica gel or by using a fibreglass mat (absorbent glass mat accumulator - AGM)

This classification according to battery chemistries is used to give information on specific storage requirements (see chapter 6.4) and on specific treatment requirements.



Fig. 10: Bad examples of used lead batteries collection<sup>25</sup>

### 6.3. Transport of used lead batteries

Used lead-acid batteries must be considered as hazardous wastes when transport is needed. Again, the main problem associated with battery transport is the electrolyte, which may leak from used batteries, requiring control measures in order to minimize the risk of spillage and define the specific actions to be taken in event of an accident:

- (a) used batteries must be transported inside containers: no matter which mode of transport is being used, i.e. boat, train, etc., used lead-acid batteries must be transported inside sealed containers due to the risk of leakage, which may be high even if the batteries are appropriately transported in upright position. The transport may displace the batteries from their original positions, including eventual box breakages or turning them

- upside down, which will certainly leak the electrolyte content, thus making it necessary to provide a shock resistant and acid resistant sealed container;
- (b) containers must be well packed to the transport vehicle: containers should not be allowed to move while being transported. Therefore, they must be bound, shrink wrapped or stacked properly to avoid this problem;
- (c) the transport vehicle should be identified with symbols: the vehicle, whether it is a ship a truck or a van must be correctly identified, following international conventions, symbols and colours, identifying the fact that corrosive and hazardous products are being transported;
- (d) specific equipment: a minimum set of equipment necessary to combat any simple spillage or leakage problems should be provided and the transport team trained on how to use it;
- (e) drivers and auxiliaries should be trained: people dealing with hazardous wastes should always be trained in emergency procedures, including fire, spilling, etc. and how to contact emergency response teams. Besides this, they should be aware of the specific kind of hazardous material is being transported and how to deal with it;
- (f) personal protection equipment: PPE should be provided for the transport team and they should be trained in the use of the equipment, in case of any accident;

- (g) transport schedule and map: if possible, hazardous waste transport should always choose routes that minimize the risk of possible accidents or other specific problems. This is made possible if they follow a certain predefined path and restrict themselves to a known schedule<sup>1</sup>.

Every transport should be controlled by state authorities (Regional Districts) by the means of permits. It is recommended the permit should contain the following minimum information:

- Name and identification of sender receiver (address, ID number, statutory or other responsible person)
- Name and identification of receiver (address, ID number, statutory or other responsible person, method of next waste management – storage, treatment, recycling, disposal)
- Name and identification of transporter (address, ID number, statutory or other responsible person)
- Amounts of transported waste
- Identification of the transported waste (waste code or other identification including indication of hazardous characteristic)
- The duration of the permit

It is strongly recommended to authorise the transporters (companies providing transport of hazardous wastes) by the Ministry of Environmental Affairs.

The transport must be realised only in vehicles that meet safety requirements. The vehicle must be labelled.





Fig. 11: Labelling of hazardous cargos according to ADR

The vehicle must be furnished with first-aid set, set for elimination of accident consequences and the driver must be instructed on techniques in the case of accident.



Fig. 12: Packaging of used lead batteries ready to transport – good example  
Source: <http://www.blacksmithinstitute.org/blog/?tag=ulab>



Fig. 13: Improved packaging – steps need to be done to reach good example  
Source: ABRI,<sup>26</sup>

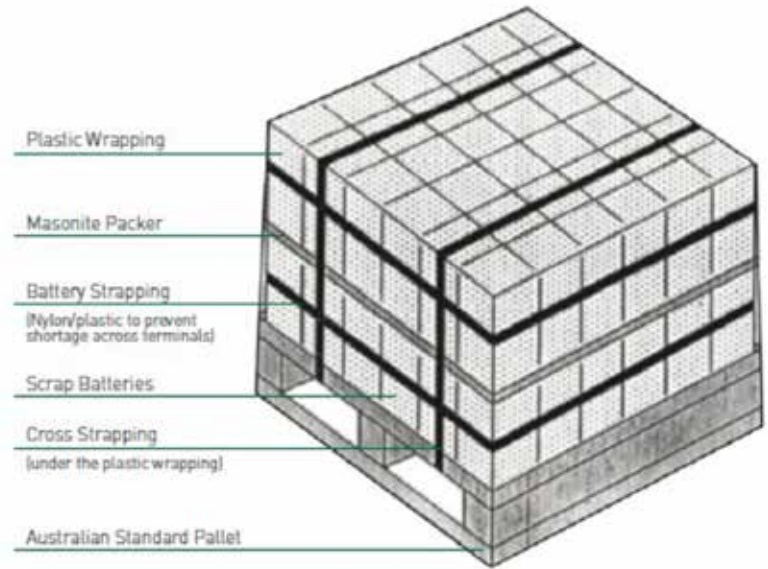


Fig. 14: Good examples of used lead batteries transport. Source: Responsible recycling of used lead acid batteries, How to manage the environmental, financial and reputational risks, Australian Battery Recycling Initiative, ABRI<sup>26</sup>

#### 6.4. Storage of used lead batteries

Storage, including temporary storage, of waste batteries at treatment facilities shall take place in sites with impermeable surfaces and suitable weatherproof covering or in suitable containers. Table 8 shows recommendations on breaking down these requirements to a more detailed specification<sup>15</sup>.

These specifications are valid for storage at treatment facilities including sorting facilities and storage facilities.

##### Storage buildings<sup>10</sup>

Storage buildings are used for storing all kinds of substances, from drums with flammable liquids, cylinders with pressurised gas, to packaged products such as chemicals and pesticides or chemical wastes awaiting disposal. They can be a standalone building or be part of another building.

Good design and construction of storage buildings containing dangerous materials focuses on events such as fire, explosion and releases of dangerous substances, in particular to prevent or control them as much as possible. Also good management practices and operational procedures are important.

Mostly, but not always, storage buildings are constructed from non-combustible materials. The degree of fire-resistance offered by the building itself determines the minimum distance to other buildings

and to the boundaries of the danger zone.

With a sufficient degree of fire resistance the storage building can be part of another establishment.

The storage space can be separated into different compartments for storing different types of hazardous material each by partition walls or by leaving a storage-free zone empty between the compartments. Some warehouses have an inbuilt store within the main warehouse. This interior store can be used to store particularly hazardous materials, such as highly flammable liquids or gases as well as peroxides.

The floors of the building are usually made of non-combustible material, are liquid-tight and are resistant to the stored substances.

The roof of the building is resistant to wind-blown fires, with the roof structure being of a fire resistant construction to prevent fire entering the store. The degree of fire-resistance depends on different factors such as, how close the store is to the border of the site or other buildings and the type of substances stored.

A storage building is normally equipped with adequate ventilation to prevent the formation of an explosive gas mixture from leakages and to extract any harmful or unpleasant fumes.

The use of electrical equipment can generate sparks that might ignite a fire in the storage building. Therefore, it is important to use explosion-protected

electrical equipment. However, proper earthing of the steel structure also may be sufficient.

If a fire breaks out in a storage facility, part of the stored substances may be released.

The storage facility should be constructed in such a way that the released substance cannot cause any harm. In particular provisions are to be taken to prevent polluted extinguishant from entering the soil, the sewage systems or surface water.

In principle, measures and provisions for storing dangerous (packaged) materials outside do not differ from those for storage inside a building. The amount and type of substances stored

determines the minimum distances from boundaries and buildings to be observed. To protect the storage from direct sunlight and rain, the storage area may be covered by a roof.

The provisions for collecting of spilled substances and possibly released extinguishant are the same as those applied in storage buildings as described above. When the storage is not covered with a roof, provisions for the cleaning of possibly polluted rainwater and its controlled discharge should be in place.

The level of fire prevention and fire-fighting measures depend on many factors, such as the flammability of the stored substances, the flammability of the packaging and the quantity of material stored.



Fig. 15: Improved Storage Facility in Central America and the Caribbean<sup>25</sup>. Outside storage (storage yards)<sup>10</sup>

Table 8: Proposal for the specification of the possible treatment requirement: "Impermeable surfaces and suitable weatherproof covering"<sup>15</sup>

Proposed Specifications for Waste Battery Storage	Applying to batteries:	
	containing liquids	other
Surfaces in operational areas should be resistant to chemicals and fire	yes	yes
Storage of waste batteries at treatment and recycling facilities should take place in a proper building or a covered place with the following minimum recommended requirements:  - Impermeable and acid and/or alkali resistant floor depending on the electrolyte used  - Efficient water collection system which directs spilled liquids towards the effluent or electrolyte treatment plant	yes  yes	no  no
Storage in a proper building or under cover should also be applied to any container that is pending, sampling or emptying.	yes	yes
Storage may be carried out without cover if the stored waste batteries and containers are not affected by ambient conditions (such as sunlight, temperature, water)	yes	yes
Covered areas should have adequate provision for ventilation.	yes	yes
Containers holding substances that are known to be sensitive to heat, light and water, and thus may stay under cover and protected from heat and direct sunlight, are to be available in sufficient quantities and should have free access to appropriate storage areas.	yes	yes
For storing quantities of more than 2,500 litres or kilograms of dangerous substances a storage building and/or an outdoor storage area covered with a roof should be used according to the BREF on Emissions from Storage [10]	yes	yes
For storing quantities of less than 2,500 litres or kilograms of dangerous substances, at least a storage cell should be used according to the BREF on Emissions from Storage [10]	yes	yes
Batteries with alkaline and acidic electrolyte shall be stored separately	yes	no

The limit of 2,500 kilograms introduced in Table 8 as the recommended threshold for requiring a dedicated storage building should be applied to collection facilities like stores, car repair centres etc. where batteries and accumulators are taken back from final users. In these facilities batteries and accumulators are stored until a pick-up service transports them to treatment facilities. Used lead batteries can be stored only in special storehouses designated for storage of hazardous wastes. The place for storage must be covered and the floor must be made from acid-resistance materials. It is forbidden to store used lead batteries near heating sources or fire because the danger of explosion is present. It is also forbidden to smoke or use open fire in the storehouse. The storehouse must be equipped with air exhaustion system. The storehouse must be connected to sewage system or retention tank.

The used batteries must be placed to double-bottom containers or the storehouse must be constructed as the catch tank or the containers must be placed into the catch tank to prevent the leakage of the electrolyte. The storehouse as well as the containers with waste batteries must be marked with notice containing information on waste type, hazardous properties and first-aid instructions. The first-aid set must be placed in the storehouse (close to the door easily available). The mobile storehouse can be used but the temperature of the ambient air must be measured because the temperature over 40°C can cause the danger of spontaneous explosion. It is recommended to regulate the requirements for storage of hazardous waste by legislation and to submit special permits for storage of hazardous waste by authorities (Regional



Fig. 16: Mobile storehouse of hazardous wastes

Districts).

The intention is that this small scale storage for portable batteries and accumulators does not need a permit for the storage of hazardous wastes, as long as the batteries are not stored longer than one year (interim storage).

The interim / small scale storage for portable batteries and accumulators has to fulfil technical requirements such as:

- suitable containers are to be used (see Table 9),
- all storage areas have impermeable surfaces (see Table 8),
- the storage building and/or the outdoor storage area are covered with a roof (see Table 8),
- the storage building or area is inaccessible for unauthorised person.

In addition

- an interim storage for portable batteries and

accumulators must be limited to the storage of this type of batteries;

- it shall also be limited by a maximum storage quantity and/or a maximum storage time of the average turnover of batteries.

Proposed limits are:

- a maximum storage quantity of 7,5 t (amount for a full 'medium-size' truck),
- a maximum storage time of 1 year;
- this interim / small scale storage facility should fall under the same inspection requirements as the regular storage facilities which need permits.

Table 9 shows recommendations on which requirements should be fulfilled in order to make a container suitable for waste battery storage<sup>15</sup>.

Table 9: Proposal for the specification of the minimum treatment requirement: "suitable containers"<sup>15</sup>

Proposed Specification for a Suitable Waste Battery Storage Container	Applying to batteries:	
	containing liquids	other
Storage must take place in leak proof containers that are acid and/or alkali resistant depending on the electrolyte used.	yes	no
Use UN standardized containers	yes	yes
Containers must be clearly labelled as regards the nature of the waste and the relevant danger symbols	yes	yes
If appropriate, the use of re-usable packaging (drums, containers, IBCs5, pallets, etc.) should be maximised.	yes	yes



## TREATMENT OF USED LEAD BATTERIES

The treatment of used lead batteries is sometimes called wet technology, as the liquid electrolyte is present.

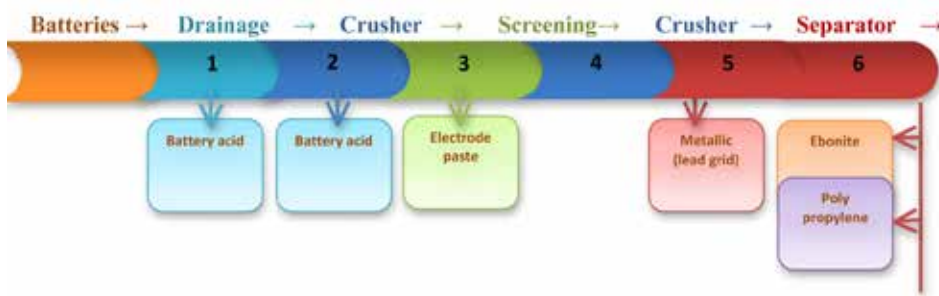


Fig. 17: Typical used lead batteries recovery process<sup>7</sup>

The Technical Guidelines<sup>1</sup> describes following treatment steps and two methods in order to isolate the metallic lead from this mixture that may be applied:

- battery breaking – including a description of processes and potential sources of environmental contamination,
- lead reduction including a description of pyrometallurgical (also known as fusion-reduction method) and hydrometallurgical methods (also known as electrolytic method) and potential sources of environmental contamination,
- lead refining - especially describing pyrometallurgical refining and potential sources of environmental contamination.

The battery scrap obtained from the breaking process is a mixture of several substances: metallic lead, lead oxide (PbO), lead sulphate (PbSO<sub>4</sub>) and other metals such as calcium (Ca), copper (Cu), antimony (Sb), arsenic (As), tin (Sn) and sometimes silver (Ag)<sup>1</sup>.

As pollutants which potentially are emitted from the treatment processes e.g. electrolyte, dust, sulphur dioxide (SO<sub>2</sub>) are described and some measures for pollution prevention are mentioned.

Relevant requirements for lead-acid accumulators derived from the Technical Guidelines<sup>1</sup> are included in Chapter 10.2 - Special care on batteries and accumulators with liquid electrolyte and Chapter 6.2 -

Treatment requirements with regard to the battery chemistry.

### Requirements for removal of fluids

According to the EU Batteries Directive (2006/66/EC) Article 12(2) and Annex III, Part A<sup>9</sup>, waste battery treatment shall, as a minimum, include removal of all fluids and acids. Table 10 specifies specifications for removal of fluids and acids as recommended in [15] in order to limit the environmental impact of these processes.

In specific cases the removal of fluids is not feasible, e.g. if the electrolyte is solidified (lead acid gel accumulators). In such cases the recycling process must be optimised individually with the aim to minimise emissions and hazards to human health as well as to achieve high recycling efficiency. During the treatment processes the environmental hazard must be taken into account. The collecting vessel must be acid-resistant, usually having special pavestone bottom and walls covered by resistant

Table 10: Proposal for the specification of the minimum treatment requirement: "Removal of all fluids and acids, their collection and treatment"<sup>15</sup>

Proposed Specification for the Removal of Fluids and Acids from Waste Batteries	Applying to batteries:	
	containing liquids	other
Batteries should be drained and prepared for recycling by adequately trained workers wearing personal protection.	yes	-
In operational areas a ground cover has to be utilised that may retain any leakage and direct it to a collecting container from where it can be removed.	yes	-
The capacity to retain leakage must at least be equal to the amount of liquid stored	yes	-
Surfaces of operational areas, drainage systems and other subsurface structures should be maintained, including applying measures to prevent or quickly clear away leaks and spillages.	yes	-
Electrolyte should be directed to appropriate treatment (recycling/recovery or appropriate waste treatment)	yes	-
Recycling/recovery of electrolyte should be done if appropriate; direct discharge of neutralised and/or untreated electrolyte should be avoided.	yes	-
When applying a neutralisation process customary measurement methods have to be used.	yes	-
Neutralised waste water from the neutralisation process has to be stored separately	yes	-
A final inspection of the neutralised waste water from the neutralisation process has to be performed	yes	-



foil and stainless steel. The space around collecting vessel is monitored for leakage. The main environmental issues of the lead industry are air and water pollution and the generation of hazardous wastes. The facilities generally have their own wastewater treatment facilities and wastewater recycling is usually practised. Many wastes are reused but the major item is leach residue that has a high environmental impact. Some local aspects, like noise, are relevant to the industry. Due to the hazardous nature of some solid and liquid waste streams, there is also a significant risk for soil contamination. As it is not purpose of the guidelines to describe into the detail some technical specifications but the waste management it is recommended to follow guidelines<sup>14,24</sup>.

## RECOVERY OF USED LEAD BATTERIES

The recovery of secondary lead consists of smelting, refining and doping.



Fig. 18: Typical used lead batteries recovery process<sup>10</sup>



Fig. 19: Secondary lead installation of the company Mach Trade (Slovakia)



Fig. 20: Costa Rica – Pb Metals SA<sup>25</sup>.

Recovery of lead from products of wet technology is operated in metallurgy part of the technology.

There are two main types of process for the recovery of lead from automotive batteries:

- a. Batteries are drained of acid and fed whole into a blast or shaft furnace (Varta process). Whole batteries and fluxes are fed into a blast furnace via a seal and oxygen enriched air is used in the blast. Antimonial lead bullion is produced, along with silica based slag and a lead/iron matte that can be recovered in a primary lead smelter. Organic components in the furnace off-gases are oxidised in an after-burner and the gases are then cooled and filtered in a fabric filter. The filter dust is dechlorinated and returned to the furnace.
- b. Batteries are drained of acid broken and separated into various fractions using automated proprietary equipment (MA and CX processes). Both the MA and CX

(Engitec) processes use hammer type mills to crush the whole batteries. The crushed material then passes through a series of screens, wet classifiers and filters to obtain separate fractions containing metallic components, lead oxide sulphate paste, polypropylene, non-recyclable plastics and rubber and dilute sulphuric acid. Some processes use a second milling stage before the plastic fraction is finally treated. Polypropylene is recycled as far as possible. The sulphuric acid drained from the batteries is neutralised unless there is a local use for it and the sodium sulphate produced can be re-crystallised and sold. These are strongly market dependent options.

As it is not purpose of the guidelines to describe into the detail technical specifications of the lead recovery metallurgical processes but the waste management it is

recommended, however, for more details to follow chapter 5.2 Best Available Techniques Reference Documents of the European Commission where BREFs contain many specifications which are relevant for waste battery treatment. Nevertheless, several alternatives are used to deal with the sulphur contained in the battery materials from the environmental point of view.

- Prior to smelting, the lead sulphate paste may be de-sulphurised by reaction with sodium carbonate or sodium hydroxide (in the

CX and related processes).

- Lead sulphate can be separated and sent to an installation capable of treating the sulphur content in the gases for example one of the direct smelting primary lead processes.
- The sulphur may be fixed in the slag or as a Fe/Pb matte. Paste de-sulphurisation prior to smelting can reduce the quantity of slag produced and, depending on the smelting method used, the amount of sulphur dioxide released to the air.

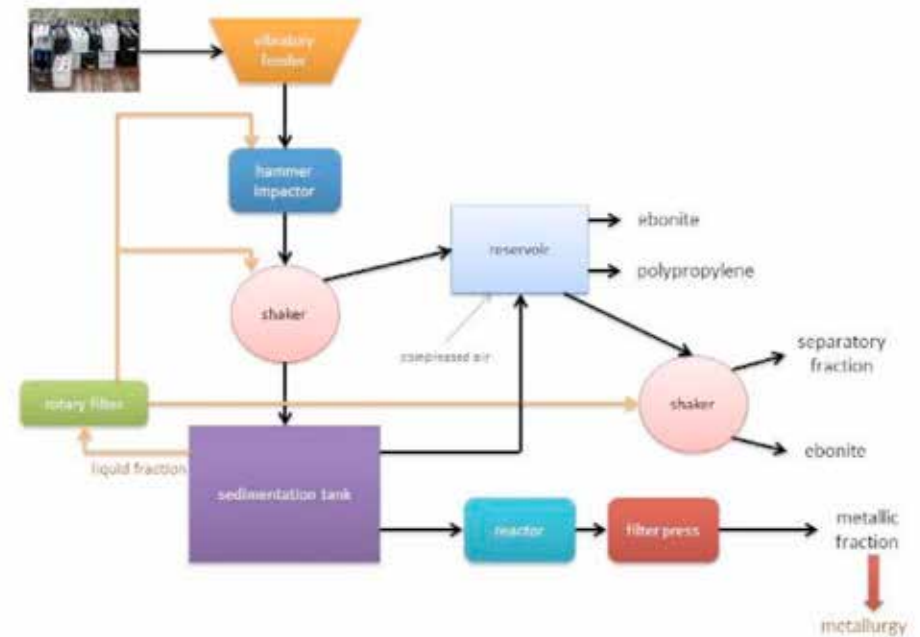


Fig. 21: Example of scheme of the wet treatment technology (Engitec)<sup>16</sup>

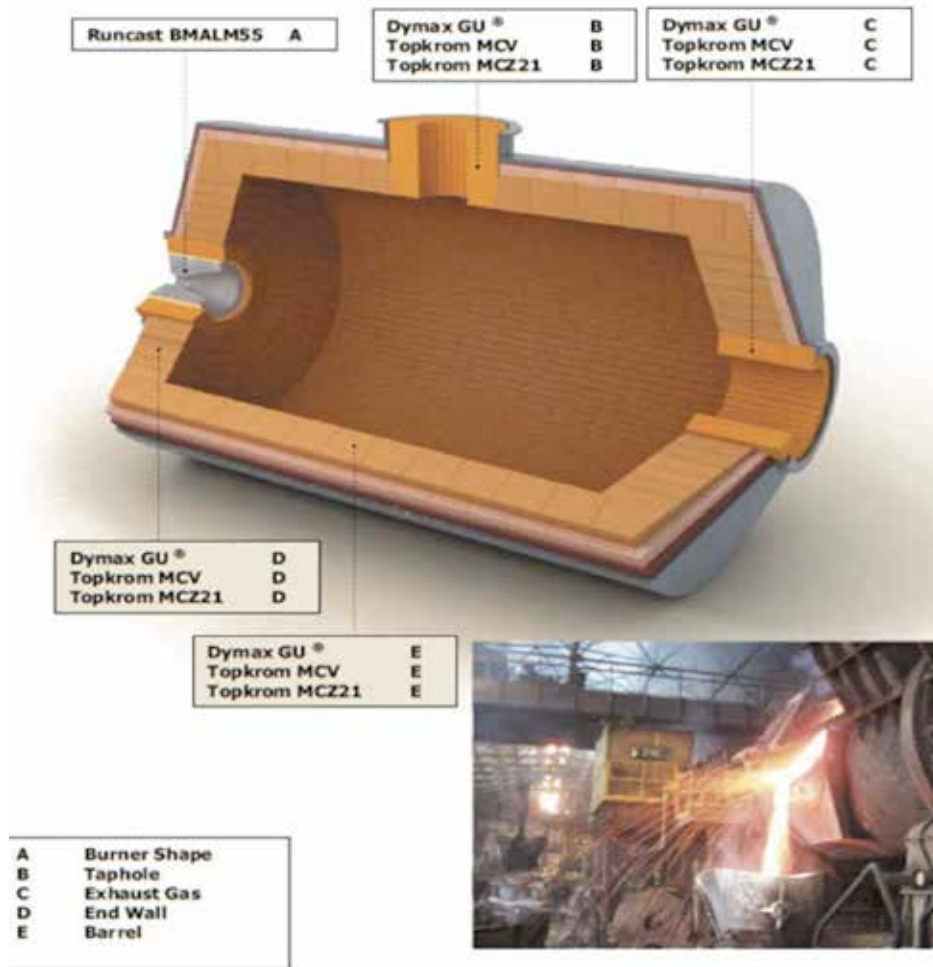


Fig. 22: Example of lead rotary furnace<sup>27</sup>

The lead and lead paste are transported to the smelting reactor that can be:

- rotary furnace,
- reverberatory furnace and blast or electric furnace,
- rotary kiln,
- ISA Smelt furnace,
- electric furnace.

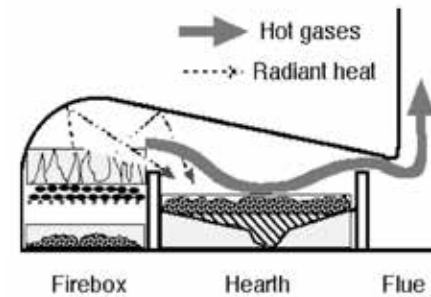


Fig. 23: Example of reverberatory furnace<sup>28</sup>



Fig. 24: Examples of blast furnace<sup>29</sup>



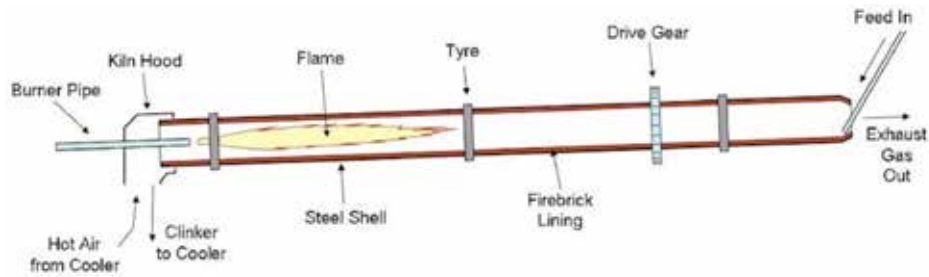


Fig. 25: Example of rotary kiln <sup>30</sup>.



Fig. 26: Example of ISA Smelt furnace <sup>31</sup>.

Rotary and reverberatory furnaces can be either gas or oil fired. Oxygen enrichment is used in several installations. Smelting is usually carried out in batches, slag and metal are tapped out separately and batches of slag are treated to recover more lead and

produce a slag that is stable. The bulk of the sulphur in the charge is fixed in the slag, which is a sodium-iron-sulphur compound with small amounts of lead and other metals.

In the ISA Smelt process de-sulphurised

paste and reductant are continuously fed into the furnace and lead bullion is tapped periodically. When the process vessel contains the maximum volume of slag, reductant and fluxes are added to produce high antimony bullion and a discard slag. The slag may also be reduced in a separate furnace. The electric resistance furnace is used for complex secondary materials and uses an open slag bath covered by coke. Raw materials are fed onto the top of the bath where they react to produce metal and slag,

which are tapped periodically. The waste gas contains CO and is burnt and flue dust is collected.

The furnace is fed with input materials that are lead metal and lead pasta, resp. dust outlet, slag formers, reductant and calcinated soda. After feeding the input opening is closed and the furnace is heated. After the smelting the content of furnace is poured out to pre-heated mould. The slag remains in the top part of the mould and the lead is pin down to ingot mould <sup>10,11,16</sup>.



Fig. 27: Furnace of Industrias Meteoro S.A. - Dominican Republic <sup>25</sup>.

The following tables give input and output balances for some lead plants in Europe as an example <sup>11</sup>.

After the recovery of lead from battery scrap the refining of crude lead is operated. Lead bullion may contain varying amounts of

Table 11: Example of input and output data for a battery recovery plant without de-sulphurisation

Input			Output		
<b>Melting materials</b>	<i>t/t Pb</i>	<i>2.12</i>	<b>Products</b>		
Battery scrap	%	63	Lead and lead alloys	<i>t/t Pb</i>	1
Other melting materials	%	21	Battery paste	<i>t/t Pb</i>	0.5
Bullion, scrap lead	%	16	Polypropylene	<i>t/t Pb</i>	0.07
<b>Reagents</b>	<i>t/t Pb</i>	<i>0.14</i>	<b>Residues</b>		
Steel borings	%	46	Residual plastics	<i>t/t Pb</i>	0.10
Petrol coke	%	32	Slag	<i>t/t Pb</i>	0.23
Soda	%	22	<b>Others</b>		
Others			Exhaust gases	<i>Nm<sup>3</sup>/t Pb</i>	70 000
Electric energy	<i>MWh/t Pb</i>	0.26			
Natural gas	<i>MWh/t Pb</i>	1.19			
PP chips (external)	<i>t/t Pb</i>	0.04			

Table 12: Example of input and output data for a battery recovery plant with de-sulphurisation

Input			Output		
<b>Melting materials</b>	<i>t/t Pb</i>	<i>1.41</i>	<b>Products</b>		
Battery scrap	%	79.0	Lead and lead alloys	<i>t/t Pb</i>	1
Other melting materials	%	3.8	Sodium sulphate	<i>t/t Pb</i>	0.096
Bullion, scrap lead	%	16.6	Polypropylene	<i>t/t Pb</i>	0.051
Flue dust incinerator	%	0.6	<b>Residues</b>		
<b>Reagents</b>	<i>t/t Pb</i>	<i>0.307</i>	Residual plastics	<i>t/t Pb</i>	0.108
NaOH	%	49.8	Metallurgical slag	<i>t/t Pb</i>	0.18
Steel borings	%	9.4	<b>Others</b>		
Petrol coke	%	17.6	Exhaust gases	<i>Nm<sup>3</sup>/t Pb</i>	37 000
Soda	%	23.1			
Others					
Electric energy	<i>MWh/t Pb</i>	0.20			
Natural gas	<i>MWh/t Pb</i>	0.73			
Steam	<i>MWh/t Pb</i>	0.84			

copper, silver, bismuth, antimony, arsenic and tin. Lead recovered from secondary sources may contain similar impurities, but generally antimony and calcium dominate.

There are two methods of refining crude lead:

- a) electrolytic (hydrometallurgical method) refining, which refining uses anodes of de-copperised lead bullion and starter cathodes of pure lead,
- b) pyrometallurgical (also known as fusion-reduction method) refining that consists of a series of kettles, which are indirectly heated by oil or gas.

electrically and selectively reduce all lead compounds to metallic lead, such as in the PLACID technology.

The chemical concept behind the electrolytic process is the conversion of all lead compounds into a single chemical species, lead in oxidation state +II (Pb<sup>2+</sup> or plumbous lead) in this case, which is then electrolytically reduced to produce metallic lead. The electrolysis deposits lead as dendrites or sponge, which are subsequently shaken off and collected on a conveyor belt and pressed to form platelets of pure lead (99.99%), which can then be conveyed to a melting kettle for casting into ingots. The whole extraction process can be run continuously 24 h/d, without interruption.

**Hydrometallurgical Methods**

The objective of the hydrometallurgical methods, or electrolytic methods, is to

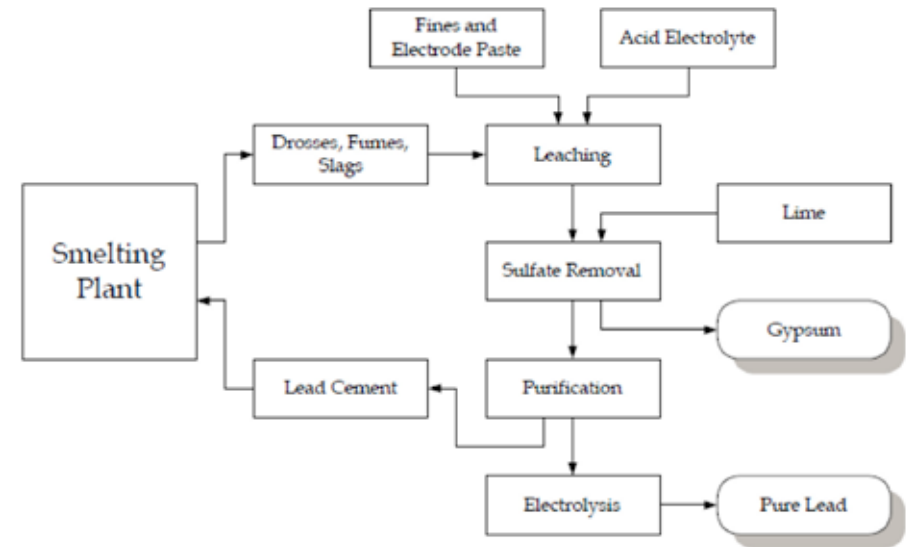


Fig. 28: Diagram of an electrolytic lead process<sup>1</sup>.

Although it may be sometimes costly when considered as an isolated plant, this process provides good results when linked to a low temperature smelting plant since, with the

appropriate separation of raw materials, it is a technological solution to overcome the lead refining processes<sup>1</sup>.

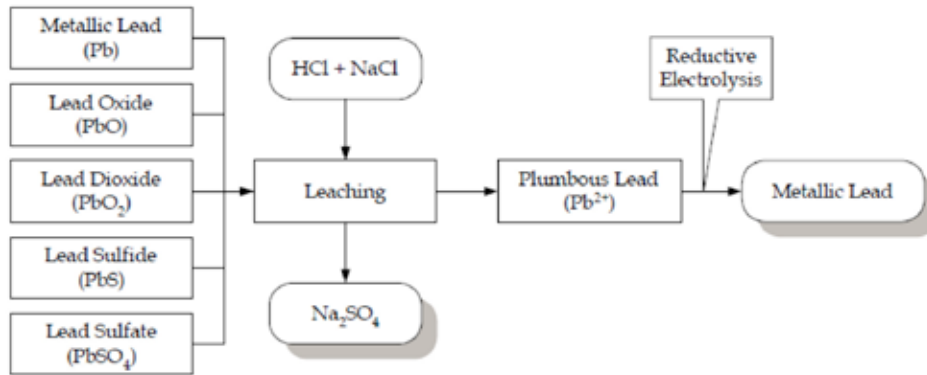


Fig. 29: Electrochemical process in hydrometallurgical lead production<sup>1</sup>.

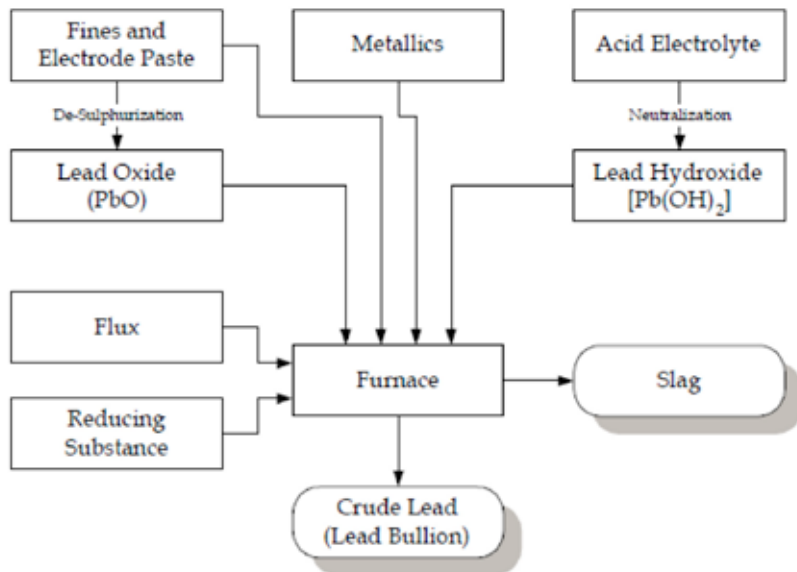


Fig. 30: Diagram of a lead smelting pyrometallurgical process<sup>1</sup>.

### Pyrometallurgical Methods

The objective of the pyrometallurgical methods (fusion-reduction) is to chemically reduce all metallic compounds to their metallic or reduced forms by means of heating and providing adequate fluxing and reducing substances.

Prior to smelting, some methods may be employed to de-sulphurise the lead sulphate paste by reacting it with a mixture of sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) and sodium hydroxide ( $\text{NaOH}$ ), such as in the CX and related processes, converting the lead sulphate ( $\text{PbSO}_4$ ) to lead oxide ( $\text{PbO}$ ). Sometimes the de-sulphurizing agent may also be iron oxide ( $\text{Fe}_2\text{O}_3$ ) and limestone ( $\text{CaCO}_3$ ). This procedure reduces the amount of slag formation and also, depending on the smelting method, the amount of sulphur dioxide ( $\text{SO}_2$ ) released into the air. However, other methods simply add controlled amounts of lead sulphate as well as de-sulphurizing agent directly into the furnace. The acid electrolyte must also be treated before its lead content may be sent to the smelting furnace. This is carried out by neutralization of the electrolyte solution with sodium hydroxide, which precipitates the present lead as lead hydroxide [ $\text{Pb(OH)}_2$ ]. This compound is then removed by decantation or filtration and directed to the furnace. The remaining solution, sodium sulphate diluted in water ( $\text{Na}_2\text{SO}_4$ ), may be further purified and the salt isolated in high

purity grades (up to food grade quality).

The metallic fraction and the lead compounds derived from the de-sulphurization and neutralization processes are then added to the furnace and smelted with fluxing and reducing agents. The necessary heat is provided by several sources depending on the specific method oil, gas, coke, electricity, etc.

The fluxing agents, which melt at a temperature below the lead compounds melting temperature, are added not only to reduce the lead smelting temperature, but also to provide a liquid solvent, which traps several unwanted compounds during the smelting and reducing processes. As the flux starts to be contaminated with all sort of impurities from the smelting process the formation of slag also starts. The physical and chemical properties of this slag, which are important characteristics to be considered in a later treatment, are entirely dependent on the chemical composition of the flux that is used.

Reducing agents, on the other hand, are added with the purpose of reducing the lead oxide ( $\text{PbO}$ ) and hydroxide [ $\text{Pb(OH)}_2$ ] to metallic lead. It is usually a carbon based compound such as coke, coal fines or other natural carbon source.

After the process had been properly balanced, the melted metallic lead starts to accumulate in the bottom of the vessel. However, as mentioned earlier, it is sometimes heavily contaminated with other

metals of economic value. Therefore, this lead bullion must undergo a refining process before pure lead can be recovered from it<sup>1</sup>.

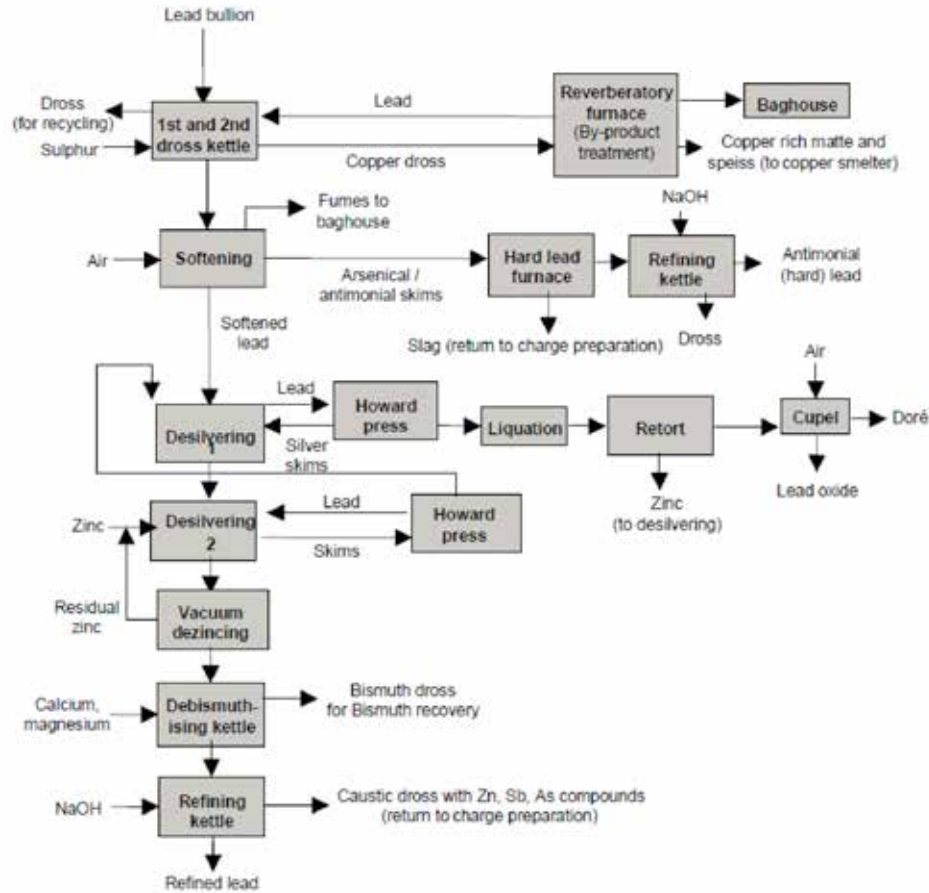


Fig. 31: Diagram of more detailed lead refining process<sup>11</sup>.



Fig. 32: Lead bars as the final product

The process of lead scrap recovery produces emissions to air and waste waters. The main emissions to air are [7]:

- sulphur dioxide SO<sub>2</sub>, other sulphur compounds and acid mists;
- oxides of nitrogen NO<sub>x</sub> and other nitrogen compounds;
- metals and their compounds;
- dust;
- VOC's and PCDD/F [11, 14].

Table 13: Example of mass release of metals from battery scrap recovery in some plants in Europe <sup>7</sup>

Process	Production (tons)	Dust (g/t <sub>product</sub> )	Zn (g/t <sub>product</sub> )	Pb (g/t <sub>product</sub> )	Cd (g/t <sub>metals</sub> )	As (g/t <sub>metals</sub> )
<b>Battery – Whole (shaft)</b>						
-process	49 000	10 - 25	0.1	2.5	<0.1	<0.15
-refinery	53 000	0.49	NA	0.024	NA	NA
-secondary*		<2 mg/Nm <sup>3</sup>	NA	<0.01 mg/Nm <sup>3</sup>	NA	NA
<b>Battery – de-sulphurised paste</b>						
-process	43 000	1 - 3	NA	0.1 - 1	0.01	0.18
-refinery	52 000	4	NA	0.5	0.02	0.24
-secondary*		6	NA	0.3	NA	0.02
<b>Battery – Whole (short rotary)</b>						
-process	10 000	15 - 35	NA	<0.5	NA	<0.3

\*Secondary hood dedusting

Table 14: Example of national emission limits for standard conditions (dry gas) for secondary lead technology (Slovak Republic)

Pollution source	Emission limit (mg/m <sup>3</sup> )		
	Solid pollutants	SO <sub>x</sub>	NO <sub>x</sub>
Transport and handling	50		
Furnace aggregates	20	350	400
Smelting and casting	10	350	400

The battery breaking and washing stages produce an effluent which is acidic and contains lead and other metals in suspension and solution. This effluent is neutralised and the water is recycled in the process. If possible, the acid is used elsewhere. A portion is usually bled from the system to control dissolved salts. Cooling water can also arise from cooling the crushing process<sup>7</sup>.

These processes also produce contaminated

surface water and consequently this water is also treated and reused. It is common practice to discharge a bleed of this sealed water circuit after further treatment and analysis. Road and surface contamination is minimised by the frequent wet cleaning of roads, hard standing areas, lorry and by cleaning up spillages.

The quality and quantity of waste water depends on the process used, the composition of the raw materials used in

the process and the practices used by the operators. The reuse of process water and rainwater is common.

Cooling water from the granulation of slag or the cooling pond is usually recirculated in a closed circuit system.

Typical components in waste water from some processes are given in Table 15<sup>7</sup>.

Table 15: Example of typical waste water analysis <sup>7</sup>

Process	Production (tons)	Dust (g/t <sub>product</sub> )	Zn (g/t <sub>product</sub> )	Pb (g/t <sub>product</sub> )	Cd (g/t <sub>metals</sub> )	As (g/t <sub>metals</sub> )
<b>Battery – Whole (shaft)</b>						
-process	49 000	10 - 25	0.1	2.5	<0.1	<0.15
-refinery	53 000	0.49	NA	0.024	NA	NA
-secondary*		<2 mg/Nm <sup>3</sup>	NA	<0.01 mg/Nm <sup>3</sup>	NA	NA
<b>Battery – de-sulphurised paste</b>						
-process	43 000	1 - 3	NA	0.1 - 1	0.01	0.18
-refinery	52 000	4	NA	0.5	0.02	0.24
-secondary*		6	NA	0.3	NA	0.02
<b>Battery – Whole (short rotary)</b>						
-process	10 000	15 - 35	NA	<0.5	NA	<0.3

\*Secondary hood dedusting

## DISPOSAL OF USED LEAD BATTERIES

The main objective of the environmental policy in the field of used lead batteries is to maximise the separate collection, reuse lead as valuable recoverable resource and to minimise disposal of used batteries as mixed municipal waste.

According to Article 14 of the EU Batteries Directive (2006/66/EC) [9] the European Member States shall prohibit the disposal in landfills or by incineration of waste industrial and automotive batteries and accumulators. However, residues of any batteries and accumulators that have undergone both treatment and recycling may be disposed of in landfills or by incineration.

From the above, it becomes clear that waste management such as landfilling and incineration cannot be considered as an environmentally sound management of used lead batteries, not only for economic reasons but also for health and environmental reasons.

However, there are cases in which the disposal is necessary, especially when no treatment and recycling facilities exist or the fractions got from dismantling of used batteries are not suitable for consequent recovery in the country which is not the European Member States.

It is recommended to ban the disposal of used lead batteries or fractions of their dismantling. When no viable end market is available it should be permitted only in landfills or underground long-term storages that are designed and operated for disposal of hazardous wastes. Such landfills of underground storages must be authorised by national competent authorities.

It is recommended to ban the incineration of used lead batteries.

### 9.1. Landfills for hazardous wastes

Some wastes - unrecoverable wastes produced during the lead recycling process will not be recycled any further or reused and, therefore, will need a sound destination for disposal. It must be stressed that usually such wastes have lead contents as high as 2-5% and must be treated as hazardous wastes, even if the lead is not leachable, and thus requires a destination in a regulated hazardous waste landfill site.

Stabilized slag from refining steps is the major hazardous waste formation from the whole process and the sodium slag arising from the utilization of sodium carbonate does not have any use due to its physical and chemical properties, and, therefore, it is being directed to hazardous waste landfills. There are other pollution sources produced during the treatment such as effluents and electrolytes that may be treated by sodium

carbonate ( $\text{Na}_2\text{CO}_3$ ) or calcium carbonate ( $\text{CaCO}_3$ ), thus producing sodium sulfate ( $\text{Na}_2\text{SO}_4$ ) or gypsum ( $\text{CaSO}_4$ ) which, after removing lead sludges by filtration, can be further purified and sold to the cement industry or the building trade.

Thus, despite some cost increases in recycling, calcium slags have found some use as a raw material in cement production which has been employed in road building, bricks, etc., with promising results<sup>1</sup>.

In such cases of production of hazardous waste the location of the landfill for hazardous wastes must be taken into account:

- secure distance from the boundary of the future landfill site to residential and recreation areas, waterways, water bodies and water sources,
- geological, hydrological, hydrogeological and mechanical-geological conditions in the vicinity,
- the protection of nature, landscape and cultural heritage in the vicinity,
- the acceptable burden on the territory,
- possible extreme meteorological effects

and their impacts,  
f) conclusions from the environmental impact assessment study.

The landfill site shall have:

- an information board,
- an approach road to the landfill and paved carriageways at the landfill site,
- a fence and lockable gates,
- a weighing-machine,
- operating premises containing all the necessary equipment,
- fire extinguisher,
- a sealing system,
- a drainage system with a leachate collection tank,
- a drainage system for landfill gas and an installation for its use or disposal, except for landfills for wastes where landfill gas is not likely to originate,
- a groundwater monitoring system,
- a landfill gas monitoring system, except for landfills for wastes where landfill gas is not likely to originate,
- a drainage system for surface water,
- an installation for cleaning vehicles,



Fig. 33: Landfill foundation

- n) other installations necessary for operation of the landfill.

Any landfill must have a fence in order to prevent free access to the landfill. The gates must be locked outside operating hours. The system of control and access to the landfill must contain measures to prevent dumping of wastes at the landfill without a consent of the landfill operator. On landfills where an artificial sealing barrier is used, the geological substratum of the landfill, considering the morphology of the landfill, must be sufficiently stable to prevent settlement that may cause damage to the artificial bottom sealing.

During the operation of a landfill measures shall be taken to minimise effects of the landfill on the environment caused by emissions of odours and dust, wind-blown material, noise and traffic, birds, vermin and insects, formation of aerosols or fires.

The landfill must be equipped and operated in such a way that dirt from it, caused mainly by the vehicles/means of transport, is not dispersed onto public roads and the surrounding land.

At the landfill site waste shall be deposited in layers 0.3 to 0.5 m thick, which are then compacted; the working layer after compacting shall be no more than 2.0 m thick. Waste shall be compacted no later than the day following its dumping unless provided otherwise. The first layer of waste shall be deposited at the bottom of the

landfill in such a way as not to damage the sealing and drainage systems of the landfill; the first layer of deposited waste may only be compacted if it is 2 m thick; the first layer may not contain waste which could damage the base of the landfill. There shall be a suitable peripheral drainage system of suitable dimensions for the drainage of surface water from the vicinity of the landfill. Appropriate measures shall be taken at any landfill in order to control leachate and manage the leachate regime providing in particular for control of water from precipitations entering into the landfill body, prevention of surface water and groundwater from entering into the landfill waste, drainage and collection of leachate, the treatment of leachate collected from the landfill in order to comply with discharge values into the sewerage system or recipient or transport of the leachate to a suitable sewage treatment plant.

The emplacement of waste on the landfill site shall take place in such a way as to ensure stability of the waste deposited and associated structures of the landfill and the necessary construction equipment, particularly in respect of avoidance of slippages.

Landfill gas shall be collected from all landfills receiving biodegradable waste. The collected landfill gas must be treated and used to produce energy; if the landfill gas collected cannot be used to produce energy, it must be flared. The collection, treatment

and use of landfill gas shall be carried on in a manner which minimises or does not have any negative effects on the environment and human health.

The operator of the landfill must provide the monitoring of:

- meteorological data (precipitation, temperature, wind, evaporation, humidity),
- emission data (amount and composition of leakage, emissions of gases),
- measurement of quality of underground

- water (pH, TOC, phenols, heavy metals, fluorides, hydrocarbons, etc.),
- topography of the landfill.

For monitoring groundwater quality in the vicinity of a landfill site, a sufficient number of measuring points must be constructed; there must be at least three, one in the groundwater inflow region and two in the outflow region. The original values of groundwater quality must be ascertained before commencement of landfill operations.



Fig. 34: Artificial geological barrier for landfill



Fig. 35: Artificial barrier using HDPE foil for landfill



Fig. 36: Foundation of landfill

### **9.2. The underground long-term storage for hazardous wastes**

Hazardous wastes including used lead batteries can be stored in long-term underground storages as closed salt- or potash-mines in appropriate containers. The very strict controls on the accepted types of waste are undertaken at the mine in drums or bulk containers. After verification the used lead batteries, if accepted by the mine, are loaded into transit capsules for transport underground. Drums are then offloaded and stacked in their allocated safe storage areas to a maximum height determined by their contents. The location of each waste

consignment is recorded for future reference. Once each disposal zone has been filled, walls (known as stoppings) are erected between the rock salt pillars to create physical barriers between storage zones. The operation of long-term storage must be held in that way that no harm for underground water or ambient air is ensured. Usually underground mines undertake extensive research, establish detailed design and operational procedures and produce thorough qualitative and quantitative short and long-term risk assessments, all supported by complementary evidence. Thanks to the geological and hydro-geological features that so effectively isolate the underground beds of rock salt from the biosphere, even in the worst case scenario the facility is likely to have “little or no

adverse consequence” on the environment.

### **9.3. Accepting waste for disposal**

Waste may only be accepted at a landfill or a long-term storage if the waste holder presents to the operator of the landfill or a long-term storage with each delivery of waste document on quantity and type of waste delivered, a consignment note and identification notes for hazardous wastes, details about the characteristics and composition of waste in the form of report on analytical control of wastes.

At the time of delivery of the verification of whether the required waste documentation is complete and correct, verification of the data, and other conditions agreed for waste acceptance, control of quantity of waste



Fig. 37: Balancing of container at the acceptance of the waste for disposal



delivered, visual inspection of waste delivery in order to verify declared information concerning origin, characteristics and composition of waste, ensuring controlled random sampling of waste and tests and analyses of waste in order to verify given information about origin, characteristics and composition of waste and recording accepted waste must be done. The operator of the landfill or a long-term storage shall confirm the acceptance of the waste to the waste holder, indicating the date and time of its acceptance.

## TRANSBOUNDARY MOVEMENT OF USED LEAD BATTERIES

The transboundary movement of used lead batteries is subject of the Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and Their Disposal. The import and export are a matter of notification of state authorities of both exporting and importing parties according to the article 6 of the Convention.

Such notification shall contain the declarations and information specified in Annex V A, written in a language acceptable to the State of import. Every shipment must be accompanied by the documentation containing information defined in Annex V B of the Convention.

The used lead batteries are classified as "A1160 Waste lead-acid batteries, whole or crushed" with Y-code "Y31 Lead; lead compounds" and H-codes "H1 Explosives", "H8 Corrosives" and "H11 Toxic".

Entry A1160 refers to "waste lead-acid batteries, whole or crushed", while entry A1170 refers to "unsorted waste batteries excluding mixtures of only list B batteries and waste batteries not specified on list B containing Annex I constituents to an extent to render them hazardous".

The mirror entry B1090 refers to "waste batteries conforming to a specification, excluding those made with lead, cadmium or mercury". However, it can be assumed

that all marketed battery systems contain at least one Annex I constituent, namely the electrolyte (which is either an acid Y34, alkali Y35, or a solvent Y42). Regardless of this classification, waste batteries are to be classified as hazardous waste in accordance with Article 1,1,b of the Convention anyhow. Therefore every transboundary transport of waste batteries is to be notified.

If the country of import is the EU Member State it is necessary to follow requirements of Regulation on shipment of waste [18]. The used lead batteries are defined as "A1160 Waste lead-acid batteries, whole or crushed" and only import for recovery is allowed, the import for disposal is allowed only the Community and its Member States, have concluded bilateral or multilateral agreements or arrangements with the country of export or in cases on exceptional grounds during situation of crisis, peacemaking, peacekeeping or war according to the Article 41 of the Regulation. The procedural requirements are described in Article 44 of the Regulation with the requirement of prior written notification in accordance with Article 4 of the Regulation and the conditions for shipment of the waste are given by Article 44 (4) of the Regulation.

To allow the Competent Authority a full evaluation of the foreign waste treatment or recycling process the notifier of the transboundary transport should at least provide the Competent Authority with the

following (technical) information:

- Chemical composition of the wastes (data from literature, no chemical analysis required in the case of batteries).
  - A technical description of the waste treatment / recycling process including a mass flow scheme.
  - Information of the recovery (R-operation) or disposal (D-operation) of the output of the treatment / recovery process.
  - Relevant information on the license (date of expire, licensed wastes).
  - Information on emissions (reference to BAT, mandatory or plant specific emission limits, current measurements of the emission to air and/or water, type of applied emission abatement technique).
  - Existence of a quality assurance system or an environmental performance assessment.
- The Competent Authority shall scrutinize these documents and consent in the transboundary movement only if the environmentally sound treatment appears to be secured.

If the waste lead batteries are shipped into countries that signed international convention ADR [19] or RID [20] the requirements of the convention must be met.

For the transport of batteries and accumulators the European Agreement concerning the International Carriage of Dangerous Goods by Road (ADR) [19] has to be considered. This is an agreement that prescribes requirements for the

transboundary transport of dangerous goods by road vehicles. The ADR specifies detailed requirements for the transport of the different battery types e.g. batteries, wet, filled with acids.

### 10.1. General requirements for “transport” / ADR

Requirements regarding the transport of lead-acid batteries from the Technical Guideline for the Environmentally Sound Management of Waste lead-acid Batteries [1] were summarised [4] as follows:

- Used batteries must be transported inside shock resistant and acid resistant sealed containers.
- In order to prevent move of containers during transport they must be well packed to the transport vehicle (i.e. they must be bound, shrink wrapped or stacked properly).
- The transport vehicle should be identified with symbols (transport of corrosive and hazardous products).
- The container shall be labelled with UN-Number 2794 BATTERIES, wet, filled with



Fig. 38: Examples of good packaging before transport, ABRI<sup>26</sup>.

acid, electric storage, Class 8.

- A minimum set of specific equipment to combat spillage or leakage during transport must be available in the transport vehicle.
  - Drivers and auxiliaries should be trained.
  - Effective personal protection equipment is to be provided and available in the transport vehicle.
  - Transport schedule and route is to be selected in a way that reduces the risk of possible accidents.
- In principle the provisions of the ADR are applicable to the transport of waste batteries. However, according to Vol. II, clause 598 of the ADR ‘used storage batteries’ are not subject to requirements of ADR when:
- their cases are undamaged;
  - they are secured in such a way that they cannot leak, slip, fall or be damaged, e.g. by stacking at pallets;
  - there are no dangerous traces of alkalis or acids on the outside of the articles;
  - they are protected against short circuiting.

Black plastic wrap is not acceptable.



Fig. 39: Examples of bad packaging before transport, ABRI<sup>26</sup>.

(Black plastic impedes inspection by the transport driver and facility staff, who will make a judgment on compliance with environmental and dangerous goods regulations, and this standard, based on observation. For example, any liquid on or leaking from the consignment could be deemed as leaking battery acid (electrolyte). Clear plastic wrap is the best option.)<sup>26</sup>.

Polystyrene slip sheets are not acceptable

(Slip sheets must be used between the layers to minimise the potential for short circuit and post penetration. Heavy duty cardboard slip sheets are preferable to Masonite or chipboard because they are recyclable, and small spills can be absorbed and are visible. Polystyrene slip sheets are not to be used as they are difficult and costly to recycle (suppliers may incur an environmental disposal levy to cover the costs of disposing of any polystyrene received).)<sup>26</sup>.



Fig. 40: Examples of bad packaging before transport, ABRI<sup>26</sup>.

(There must be at least two vertical straps tying the load to the pallet)

(Batteries need to be wrapped as well as strapped)



Fig. 41: Examples of bad packaging before transport, ABRI<sup>26</sup>.

(Broken pallets are unacceptable)

(The pallet load needs horizontal as well as vertical strapping)



Fig. 42: Bad and unacceptable examples of transport conditions

## 10.2. Special care for batteries and accumulators with a liquid electrolyte

Batteries and accumulators with free liquid electrolyte may cause specific damage during storage and transport. They shall be kept separately based on the nature of their electrolyte (acidic, alkaline or organic) and stored in tight, leak proof and stable containers. It is recommended to use UN-tested and correctly labelled containers even for intermediate storage to avoid extensive manipulation/repackaging when the batteries are shipped.

Lead acid batteries are listed under UN-Number 2794/Class 8, alkaline batteries under UN-Number 2795/Class 8. Accumulators with an organic electrolyte until recently have not been in common use and therefore are not mentioned in the ADR. Sealed batteries/accumulators (e.g. consumer batteries type AA, AAA, C, D) are normally not regarded as batteries with liquid electrolyte. However, sealed lead acid batteries should be regarded as accumulator with liquid electrolyte since the acid may leak out quite easily due to mechanical damage. It is therefore recommended to collect, store and transport seal lead acid batteries in the same way as normal lead acid batteries.

## POTENTIAL SOURCES OF ENVIRONMENTAL CONTAMINATION

### 11.1. Battery Breaking Process

Each step of handling with used lead batteries is possible sources of contamination that may occur in the recovery processes. It is described shortly and should be understood as the predictable list of common contamination sources and where to look when searching for them. Specific sources of contamination will have to be determined in the light of the process employed.

The common sources of environmental impacts in the battery breaking process are then:

- (a) spilling batteries - acid electrolyte and lead dust contamination source: battery spillage may be a very common source of environmental contamination as well as human health injuries since the electrolyte is not only a strongly corrosive solution but also a good carrier of soluble lead and lead particulates. Therefore, if this solution spills in an unprotected area, it may contaminate the soil or injure workers. Besides, after spilling on unprotected soil, the soil itself becomes a source of lead dust once the solution evaporates and the lead becomes incorporated into soil particles which may blow by wind or raised by vehicle transit;
- (b) manual battery breaking – source of human health injury and environmental damage through heavy spillage and lead

contaminated dust formation: manual breaking usually relies on primitive tools, poorly protected workers and no environmental protection whatsoever. The situation is even worst in the case of sealed batteries, which are not easily drained, increasing dramatically the risk of heavy spillage and damage to human health.

Therefore, it should be avoided at all costs;

- (c) mechanical battery breaking – source of lead particulate: the process of breaking batteries through crushing on hammer mills may spread lead particulate. However, the fact that the mill is sealed and uses copious quantities of water the formation of such particulates is prevented;
- (d) hydraulic separations – contaminated water leakage: the hydraulic separations, both metallic from organic and heavy organics from light organics, are usually preformed inside sealed machines and with a closed water system. However, if any water leakage occurs, it will be heavily contaminated by lead compounds;
- (e) plastic and ebonite chips – contaminated wastes: ebonite scraps removed from the breaking process may pose a problem, since they are usually contaminated by levels as high as 5% (w/w) of lead. Therefore, it is important that the final traces of lead are removed by a second wash, preferably in an alkaline solution, followed by another rinse prior to further treatment or disposal<sup>1</sup>.

### 11.2. Lead Reduction Process

The common sources of environmental impacts in the pyrometallurgical lead reduction process are:

- (a) lead compounds derived from the breaking process – lead and lead compounds in dust and water: the separated and fine materials from the breaking process are usually wet, since the main processes of separation are based on water techniques. However, if they are not incorporated in a fully automated process, they will have to be transported from the breaking facility to the reduction facility and some muddy and/or watery material may spill and fall from the transport system. After drying, these materials become a powder and may contaminate the factory and its surroundings as fine lead dusts;
- (b) drosses – lead contaminated materials: drosses are formed while the fusion process takes place. Its function is to remove materials that are not easily incorporated or wanted in the crude lead. However, these drosses still contain lead that can be recovered and are recycled in the fusion process. In order to accomplish these task, the drosses must be removed and transported to the furnace charging bay, but since they are usually a dusty material and occasionally powdery (copper dross), they may be a source of lead contamination while being transported;
- (c) filters – lead contaminated dusts: furnaces need filters in order to capture lead dusts formed in the fusion process. After being

used, they are usually recycled in the same smelting process since they may contain as much as 65% of lead. However, the care and maintenance of these filters may be an important source of contaminating dust, which could pose a risk to the human health and the environment. Besides, over-used filters no longer capture lead dusts as originally intended and the dust emissions from the fusion oven becomes an important source of contamination. Finally, one must also realize that the furnace inlet is itself a source of lead dust to the environment, since it can be an open system. The high temperature fume that leaves the furnace inlet and tapping area, for example, have a high lead content, and will be readily absorbed by the human body;

- (d) sulphur dioxide (SO<sub>2</sub>) emissions – the percentage of sulphur from a given amount of lead scrap load that leaves the reduction system as sulphur dioxide (SO<sub>2</sub>) is highly dependent not only on the furnace conditions, but also in the kind of skim material being formed. As a general trend, this number may fall between 0% and 10% and it is significantly reduced if the flux used is a mixture of iron and sodium based compounds producing sodium skims and pyrites. Ebonite also has 6-10% of sulphur that may contribute to the SO<sub>2</sub> emission if it is added to the furnace charge;
- (e) organic material combustion – tar formation: a well structured and controlled refinery does not need to worry about

tar formation, since its reduction process consumes all organic materials. On the other hand, the less controlled the reduction process is, the greater are the tar emissions, especially in artisan foundries. If the reduction furnace has filters, the emission of tars is an even greater problem since they are very pyrogenic and may produce fires in the filtration plant, thus increasing the risk of an accident and the possibility of a rogue emission. The introduction of afterburners to complete the combustion of gases from the furnace is the usual solution to this problem, but a complete restructuring of the process, removal of organics for example, may present better perspectives;

- (f) chlorine (Cl<sub>2</sub>) and chlorine compounds emission: an initial separation of the materials allowed to enter the reduction process reduces the chlorine emission considerably. Cl<sub>2</sub> is source for PCDD/PCDF formation during lead smelting thermal process (see chapter 5.4). However, increasing amounts of PVC in the furnace increases the chances of chlorine emissions. The major part of it is absorbed by the basic skims of calcium or sodium, however some of the chlorine is chemically converted into lead chloride which is volatile under furnace conditions but captured by dust filters as the temperature decreases;
- (g) slag production: this is the majority of the waste production during the reduction process. As an average picture, around

300-350kg of slag is produced for each ton of metallic lead, depending on specific factors of the process and the kind of residue being formed (calcium or sodium skims), and around 5% (w/w) of this slag is composed of lead compounds. Therefore, special consideration must be given to the leachate that may be produced if an unstable water soluble slag comes into contact with water or moist air. A purpose built under cover storage bay to store this material must be planned well in advance in order to avoid human health and environmental problems<sup>1</sup>.

### 11.3. Lead Refining Process

The refining process can be a polluting process if some control measures are not taken. Some sources of environmental impacts in the lead refining process are:

- (a) over heated lead – lead fumes: sometimes the lead from the reduction process is introduced directly into the refining kettle, which may be as hot as 1,000°C. Therefore, it is not uncommon that the lead refining process produces large amounts of lead vapour. Ideally lead should be tapped from the furnace directly into a lead bath or allowed to cool prior to pouring;
- (b) sulphur dioxide (SO<sub>2</sub>) emissions: the copper removal by addition of elementary sulphur may produce large quantities of sulphur dioxide (SO<sub>2</sub>), since sulphur oxidizes readily in the presence of oxygen at the oven temperatures. The use of iron pyrites

eliminates this problem;

- (c) skim production and removal – metal contaminations: the skim production and removal from the refining kettle while refining unwanted metals from the crude lead may pose threats to the human health and environment due to the physical characteristics of the skims. Sometimes they are in the form of a very fine and dry dust with a high percentage of lead and other metals, it is important to provide adequate covered or sealed transport, storage and a sound destination to this potentially hazardous by-product;
- (d) chlorine (Cl<sub>2</sub>) tin (Sn) removal and recovery – chlorine gas release: If the tin is removed by chlorine gas for later recovery, then this is a very delicate procedure. The intake of gas is planned in order avoid chlorine release, i.e. the gas reacts with the tin before reaching the surface of molten lead. However, an uncontrolled addition of chlorine may release the poisonous gas to the environment. Besides, the storage and handling of chlorine is itself a delicate operation due to its corrosiveness and toxicity;
- (e) oxygen (O<sub>2</sub>) enriched air tin (Sn) removal – lead fume: while the air is being passed inside the molten metal, the nitrogen (N<sub>2</sub>) present in the air does not react. The consequence of this is that the gas bubbles violently in the surface of the metals releasing dusts and metallic fume<sup>1</sup>.

### 11.4. Bad examples of potential contamination of the environment

## ECONOMIC ASPECTS OF ENVIRONMENTALLY SOUND



Fig. 43: Examples of bad used lead batteries management

Source: [http://www.worstpolluted.org/projects\\_reports/display/78](http://www.worstpolluted.org/projects_reports/display/78)



Fig. 44: Examples of bad used lead batteries management

Source: <http://www.blacksmithinstitute.org/blog/?tag=ulab>



Fig. 45: Examples of bad used lead batteries management

Source: <http://www.blacksmithinstitute.org/blog/?tag=ulab>



Fig. 46: Examples of bad used lead batteries management

Source: ABRI,<sup>26</sup>

## MANAGEMENT OF USED LEAD BATTERIES

The project<sup>2</sup> proposes the application of extended producer responsibility as a system for financing the environmentally sound management of used lead batteries according to the model of EU stated in the Battery Directive<sup>9</sup> The extended producer responsibility is based on the responsibility of producers / importers of batteries to establish and operate system of separate collection, treatment and recovery of used batteries what means also to finance whole system. The producers can fulfil their obligations individually or collectively through collective scheme.

Producers must cooperate with producers (holders) of used batteries, as services and maintenance facilities as well as with municipalities to provide for separate collection of used batteries in order to fulfil legal limits of collection, given usually as a percentage of amount put on the market. The industrial association or governmental authority (ministry, agency...) collects data on amount of batteries put on the market during the years by every producer / importer. Every producer / importer can calculate his market share that is a base for calculation of the collection share. The producer / importer is also obliged to fulfil recycling and recovery limits. He must cooperate also with the facilities dealing with the treatment and recovery of used

lead batteries in the country or abroad. If the price of the treatment of used batteries is minus the producer / importer must pay also the costs connected with treatment. If the producer / importer fulfil his obligation individually he has to finance the separate collection of the amount of used batteries that is equivalent to his collection share. If the producer / importer join the collective scheme then he pays to the system money equal to the amount of batteries that he put on the market and rate. The rate reflects real costs of separate collection, treatment and recovery of used batteries, as well as the costs of the information campaigns and the operation of the collective scheme itself. However, obtaining secondary lead from used lead batteries is economically attractive, cutting about 25 % from the energy bill compared with mining primary lead. In addition, batteries are a ubiquitous product with a predictable lifetime, and the large market for recycled lead creates economies of scale. As a result, battery manufacturers rely heavily on secondary lead, most of it sourced from recycled batteries. Some of the lead recycled from batteries in the informal sector, however, does not re-enter the manufacturing sector but is used instead for other purposes, such as sinkers for fishing lines. The costs of used lead batteries treatment and recovery vary according to the market situation. It is impossible to make estimation of the costs because prices in Europe are

different from the prices in other regions. The simplified scheme of waste, finance and information streams in used lead batteries EPR system is given in Figure 47.

that the lead environmentally sound management process is deeply embedded in social and economic aspects that dictate several problems as well as several solutions not covered and which could not possibly be covered in this guideline.

Last but not least, it must be understood

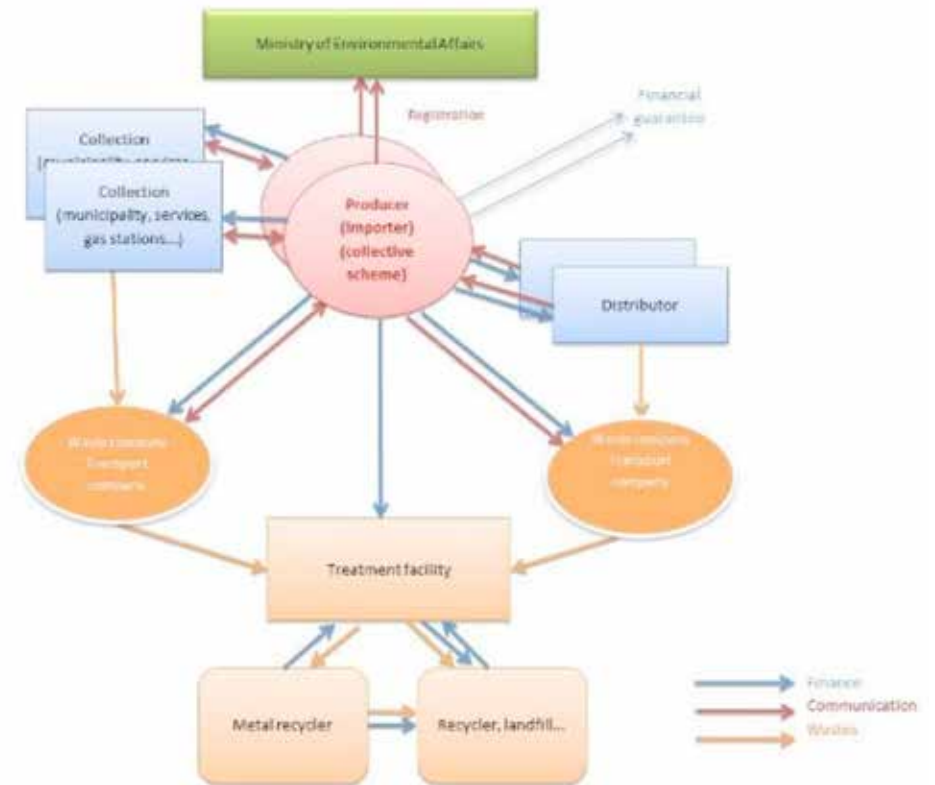


Fig. 47: Scheme of waste, finance and information streams in used lead batteries EPR system

Therefore, a specific contextual map should be generated, encompassing local politics, economical aspects, social aspects, local and international market aspects, etc., and the lead recycling plant inserted into this context. No solutions or orientations given here should be taken for granted but, instead, analyzed under the lights of this contextual map and its possibilities.

## CONCLUSIONS AND RECOMMENDATIONS

As the lead batteries are at once an important source of secondary lead and environmental danger it is necessary to operate efficient system for environmentally sound management of used lead batteries in the countries. The very effective model for used batteries is implemented in European Union based on extended producer responsibility. This model generalise sufficient financial sources that can cover all costs of separate collection, treatment and recycling of used lead batteries. This is the main assumption for building an effective system.

The first and the most important step of used lead batteries management is separate collection. It is obvious that throwing away the used lead batteries together with mixed household waste is wasting material resources and could lead to the potential burden of the environment and public health. It is recommended to collect used batteries in places of their production, i.e. in services and maintenance operations. Effective system is mobile collection when mostly batteries from households and very small operations are collected. There are also other collection systems available for used batteries collection. The efficiency of secondary lead production is depended on the sorting and treatment of used lead batteries. It is recommended to

operate treatment in the same facility and technology as recycling by metallurgical technologies but it is not the necessary condition. The treatment means dismantling of used lead batteries in order to get metals and other components. It is recommended to respect European standards for used lead batteries treatment given by BREF documents, mainly given by BREF on Non-Ferrous Metals<sup>7</sup>. European standards also cover the best available techniques for lead recycling.

Some wastes arisen during the processes of treatment and recycling cannot be recovered and they must be landfilled on special landfills for hazardous wastes. The technical and environmental conditions for landfilling of hazardous wastes are also introduced.

The necessary part of all steps of waste management is transport. As lead batteries (new or used) are hazardous and introduce danger especially for waters (surface or underground) special conditions for transport must be followed.

The system of environmental sound management of used lead batteries can be successfully implemented only when four conditions is met:

1. legislative rules are effective and applicable,
2. all or at least most of producers / importers of lead batteries are participating in the system,
3. facilities for lead recycling are available

in appropriate distance (best of all in the country or in a not-very-far distance in neighbouring countries),

4. effective state control and supervision to prevent human health and environmental hazard together with good law enforcement.

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