

DRAFT TECHNICAL GUIDELINES
ON THE ENVIRONMENTALLY SOUND MANAGEMENT
OF LEAD-ACID BATTERY WASTES

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FOREWORD

Since the 16th TWG, when these Guidelines were first presented to the Parties of the Basel Convention and to the Basel Convention Secretariat, several contributions were made in order to improve the Guidelines and its applicability. We would like to express our gratitude for these contributions since, without them, our work would be much harder than it was.

The document presented here tries to adopt a pragmatic and organized approach toward the environmentally sound management of the used lead-acid battery wastes and, in order to accomplish such approach, some modifications were made in relation to the previous versions of the document which improve the overall ease of use as well as the technical and environmental discussions.

It is our feeling that the Guidelines are now closer to its objective of helping parties and providing guidance in the environmentally management of lead-acid battery wastes.

Introduction

In most countries, nowadays, used lead-acid batteries are returned for lead recycling. However, considering that a normal battery also contains sulfuric acid and several kinds of plastics, recycling may be a potentially dangerous process when not carried out properly. These technical guidelines are, therefore, meant to provide guidance to countries which are planning to build their capacity in order to manage the lead-acid battery wastes. A comprehensive approach is adopted and clear information is provided on several issues related to these wastes and it is expected that by using these guidelines a country will be able to improve its actions in relation to the following aspects:

- protection and improvement of its environmental quality;
- protection of its population health;
- adoption of clean technologies in order to minimize waste generation;
- adoption of reuse and recycle as means to protect non-renewable natural resources;
- adoption of the environmentally sound management of used lead-acid batteries;
- creation of a sustainable and regulated system of lead utilization;
- adoption of management plans for lead wastes;
- generation of social, economical and environmental benefits through the environmentally sound management of lead wastes.

One should note, however, that no technologies will be covered in this guideline. Instead, a broader approach will be adopted while discussing general subjects regarding the lead recycling and, in order to obtain specific information on technologies, the reader is asked to consult the bibliography listed at the end of the text.

Why Recycle?

The recycling process is an essential element in the sustainable development and provides rational uses for scarce, or potentially scarce, natural resources such as lead. There are strong advantages in the recycling process:

- **extension of natural resources lifetime** – although there are undiscovered ore deposits all over the world, they are all ultimately finite and this limit is linked to its usage rate. Therefore, recycling processes extend the lifetime of these deposits;
- **reduced monetary costs** – secondary materials provide means of monetary economy by: (a) being cheaper processes than primary minerals recovery; (b) reducing the dependence on imported materials; (c) reducing the investment cost of equipment; and (d) reducing the waste production, specially the primary extraction waste;
- **energy conservation** – since few metals occur in nature as readily usable forms, the recycling processes allow the production of metals with just a small fraction of the energy used in the primary processes. Furthermore, since most of the primary metal processes require energy-expensive procedures which usually depend on fossil fuels, as in furnaces for example, the recycling processes provide means of pollution reduction;

Beside these aspects which are applied for all metal recycling processes, lead itself has some other important factors that make recycling even more environmentally sound:

- **toxicity toward the environment and human health** – it is well known the consequences of lead exposure, being it human or environmental exposure. Thus, it is reasonable to think that a lack of a lead recycling system would increase dramatically the risk of exposure since the lead waste would have to have environmentally unsound destinations;
- **large recyclability** – the fact that lead has a low melting point and it is easily refined from scrap increases its recyclability, i.e. the relatively technical ease or feasibility of lead isolation from scrap and reintroduction into the raw material stream;
- **large market** – lead enjoys a large market and a reasonably well-organized collection system, depending on the country of course, from one predominant product which has a short and predictable lifetime: the SLI battery;

From the above discussion, it becomes clear that destinations such as landfilling, incineration and others must not be considered as an environmentally sound management of lead wastes, not only for economical reasons but also for health and environmental reasons.

Once this is recognized, recycling processes become a technologically viable answer to the problem since, when properly applied and controlled, they can provide an economical healthy and environmentally sound solution. Therefore, lead recycle should be pursued as an optimal solution to the environmentally sound management of lead-acid batteries.

1. HISTORICAL BACKGROUND

The physical and chemical properties of lead such as its malleability and resistance to corrosion were already known from the ancient civilizations. Lead has been mined and smelted, indeed, for at least 8,000 years. This is confirmed by artifacts in various museums and by ancient histories and other writings, including the biblical Book of Exodus. Lead beads found in what is now Turkey have been dated to around 6.500 BC, and the Egyptians are reported to have used lead along with gold, silver, and copper as early as 5.000 BC indicating that the technology of producing metallic lead by reductive melting in the presence of carbon sources slowly spread from China to Middle East and from there to Africa along the VI and V millennia BC. In pharaonic Egypt, lead was also used to glaze pottery and make solder as well as for casting into ornamental objects. The British Museum holds a lead figure, found in the temple of Osiris in the ancient city of Abydos in western Anatolia, that dates from 3.500 BC.

One of the most important historical applications of lead was the water pipes of Rome. Lead pipes were fabricated in 3-metre lengths and in as many as 15 standard diameters. Many of these pipes, still in excellent condition, have been uncovered in modern-day Rome and England. The Roman word *plumbum*, denoting lead water spouts and connectors, is the origin of the English word plumbing and of the element's symbol, Pb. Under Constantin there was around 8.000 tons of lead pipelines in Rome and a rough estimative is that the production of lead of the Roman empire during four centuries reached 15 millions of tons.

Marcus Vitruvius Pollio, a 1st-century-BC Roman architect and engineer, warned about the use of lead pipe for conveying water, recommending that clay pipes be used instead. Vitruvius also referred in his writing to the poor color of the workers in lead factories of that day, noting that the fumes from molten lead destroy the "vigor of the blood". On the other hand, there were many who believed lead to have favorable medical qualities. Pliny, a Roman scholar of the 1st century AD, wrote that lead could be used for the removal of scars, as a liniment, or as an ingredient in plasters for ulcers and the eyes, among other health applications. Romans also knew the resistance of the lead to the corrosion and the Roman marine was a big consumer of this metal. Submarine researches in Mediterranean discovered Roman galleys with lead coated hinges and nails.

After the Roman period and during the Middle Age the exploitation and use of lead continued to develop. At this period the manufacture of pipes made progress and instead of rolling a lead sheet, manufacturers started to sink a cold cylinder with the interior diameter size into the molten metal. But pipes were not the main medieval use of this metal. It was also used as roof cover in cathedrals and buildings, in the manufacture of soldering joints, in the installation of stained-glass windows, and also find a new use after the printing discovery.

In 1859 a French physicist, Gaston Planté, discovered that pairs of lead oxide and lead metal electrodes, when immersed in a sulfuric acid electrolyte, generated electrical energy and could subsequently be recharged. A series of further technical improvements by other investigators led to commercial production of lead-acid storage batteries by 1889. The huge growth of battery markets in the 20th century (eventually consuming about 75 percent of the world's lead production) largely paralleled the rise of the automobile, in which batteries found application for starting, lighting, and ignition.

Another prominent lead product was tetraethyl lead, a gasoline additive invented in 1921 to solve "knocking" problems that had become commonplace with the development of high-compression engines operating at high temperatures. Soon after reaching its peak 50 years later, the use of this lead compound declined as the installation of catalytic converters became mandatory on the exhaust systems of passenger cars and also by environment protection laws.

Despite the constant increase of uses of the lead during the five last millennial, the consumption and the exploitation of mines only took an industrial rhythm after the XIX century. It was estimated that the lead consumption since the prehistory would hardly have passed thirty millions of tons until that time and the actual consumption is around five millions of tons per year.

2. LEAD-ACID BATTERIES TECHNICAL DATA

2.1. Concepts and Definitions

Battery: an electrochemical apparatus which provides electrical energy through the controlled use of chemical reactions. Some batteries use reversible chemical reactions and can be recharged, such as the lead-acid batteries, while others use non-reversible reactions and have just one useful life-time.

Battery capacity: amount of electricity that the battery can deliver before the voltage falls below the final limit for a charge of 10 hours. The capacity is expressed in Amperes/hour (Ah).

Box or Casing: container subdivided with intermediary walls where the individual elements will be inserted along with electrolyte.

Cap or Cover: part intended to close the box of the battery.

Cell or Electrochemical Cell: is an electrical generator constituted of at least two electrochemical reactions (called semi-cell reactions), one of them being of reductive nature and the other of oxidative nature.

Charge: operation through which electrical energy is supplied by an external electrical source and converted into chemical energy in the battery.

Connectors: metallic lead conductor used to interconnect not only the individual plates, forming elements, but also the elements between each other forming the internal electric circuit.

Electrical Accumulator: device constituted by an electrolyte, an element and a container housing them, capable of storing the electrical energy as chemical energy and release this energy when connected to an external consuming circuit. A **Lead-Acid Accumulator or Lead-Acid Battery** is an electrical accumulators 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 sulfuric acid solution.

Electrolyte: ionic conductor into which the plates are submerged. In lead-acid batteries, the electrolyte is a diluted sulfuric acid solution 36% by weight (400g of sulfuric per liter of distilled water). The charge of a battery is determined by the specific gravity or density of its electrolyte: a fully charged battery has an electrolyte with density of 1.270kg.dl⁻¹.

Element: it is a series of negative and positive plates, placed consecutively and isolated between each other with plate separators. Plates of same polarity are electrically connected. Therefore, an element may be considered as a set of electrochemical cells in parallel connection.

Negative Plate or Anode: plate where the oxidative reactions take place.

Nominal Voltage: there are two types of nominal voltage.

- **cell nominal voltage** - it is the voltage that the chemical reaction used in the battery is able to provide and, in the case of lead-acid battery reactions, this means 2V;

- **accumulator nominal voltage** - it is a function of how many cells are connected in series: car batteries usually have 6 cells in series thus providing (2V x 6 cells) 12V of nominal voltage.

Plate Separator or Spacer: component inserted between two consecutive electrical plates in a battery, made up of PVC, paper cards or other porous materials, and permeable to the electrolyte. It

is necessary to prevent metallic contact between plates of opposite polarity ensuring space between them.

Plug or Vent Cap: removable part intended to allow gases to escape and to check and maintain the electrolyte level.

Positive Plate or Cathode: plate where the reductive reactions take place.

Sealant: material used for sealing the cap of the battery box.

2.2. Description

No matter the function the battery has been planned for, a typical lead-acid battery has the following constituents:

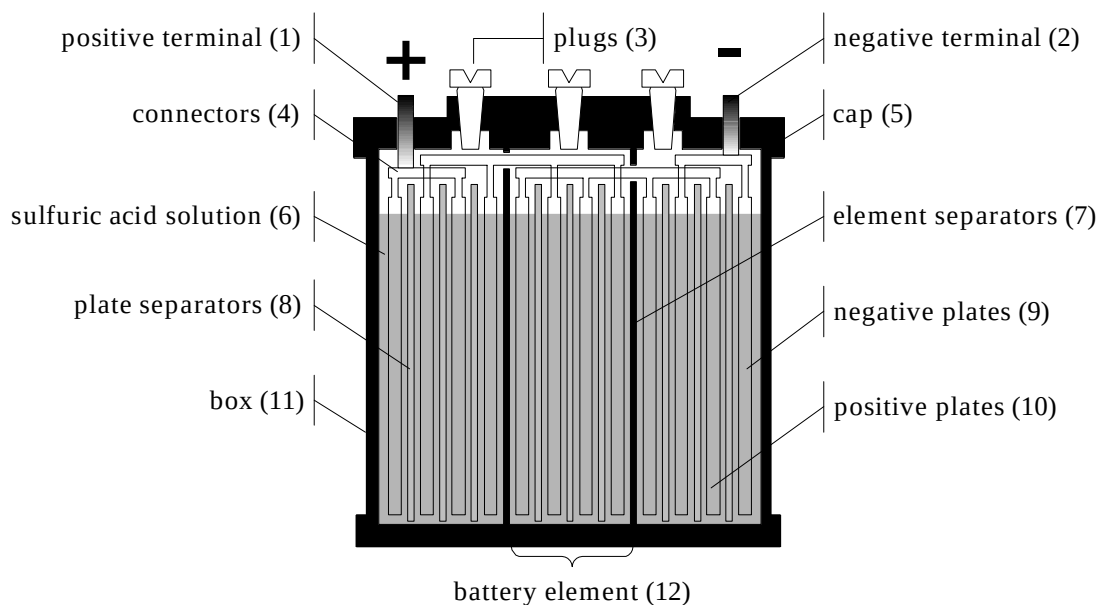


Figure 1: lead-acid battery components and internal structure

- **positive (1) and negative (2) terminals:** made of lead, and where the external electricity consumer devices are connected;
- **plugs (3):** one for each battery element, where distilled water can be replaced whenever needed and also to provide an escape route for eventual gases formed into the cells;
- **connectors (4):** made of lead, that make electrical contact between plates of same polarity and also make electrical contact between separated elements;
- **cap (5) and box (11):** usually made of ebonite or polypropylene;
- **sulfuric acid solution (6):** the electrolyte of the battery;
- **element separators (7):** usually a part of the box and made of the same material, provide chemical and electrical isolation between electrical elements. They are connected in a serial layout in order to increase the final voltage of the battery;

- **plate separators (8):** 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 (9):** constituted by a metallic lead grid covered by a lead dioxide (PbO_2) paste;
- **positive plates (10):** constituted by metallic lead plates;
- **battery element (11):** a series of negative and positive plates, placed consecutively and isolated between each other with plate separators. Plates of same polarity are electrically connected.

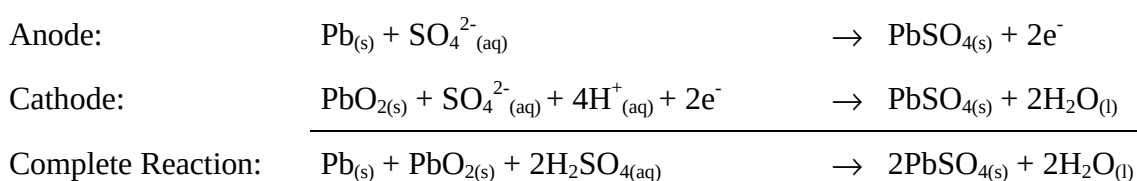
The battery plates are constituted by metallic lead structures, known as grids, covered by a lead dioxide paste, in the case of the negative plates, or by a porous metallic lead paste, in the case of the positive plates. The lead used in both the plates may also contain several other chemical elements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

After being shaped, the battery plates are so placed that each negative plate is followed by a positive plate with the interposition of a plate separator, which is made up of polyethylene, PVC or fibrous paper, and used in order to avoid short circuit between two consecutive plates. This process continues until there are 6 to 20 pairs of negative and positive plates aligned and electrically isolated. The plates of same polarity are then electrically connected and the plate sandwiches, now called battery elements, are inserted into their battery compartments. A standard battery element has 13 to 15 plates and each element is capable of producing 2volts with high amperage. The elements are then connected in series with a lead-antimony alloy connector in order to provide a higher voltage. The higher the voltage, the higher the number of elements connected: a standard automobile battery have 6 elements in series producing ($2\text{V} \times 6 \text{ elements}$) 12 V.

Finally, the battery is assembled and receives its electrolyte. The lid is then sealed and the product is examined for leaks, after which it will receive its first charge.

2.3. Operation

When the battery provides electric energy to an external device, several chemical reactions take place at the same time. At the positive plates (cathode) an reductive reaction takes place when the lead dioxide (PbO_2) is converted into lead sulfate (PbSO_4). On the other hand, in the negative plates (anode), an oxidative reaction occurs and metallic lead is converted into lead sulfate. The electrolyte, sulfuric acid (H_2SO_4), provides the sulfate ions for both semi-reactions and acts as a chemical bridge between them. For every electron generated at the anode, there is an electron consumed at the cathode, and the equations become:



While the battery discharges, operating a starting engine for example, the concentration of sulfuric acid slowly decreases from the electrolyte solution, since the sulfate ions become incorporated in the lead sulfate that is being formed in both electrodes. As the concentration of the sulfuric acid decreases from the electrolyte, the density of the solution decreases from the 1,25 kg.dl⁻¹ value, which is the density of a fully charged battery, thus making possible to determine the charge level of a battery simply by measuring the density of its solution. As the process continues, the active materials become depleted and the speed of the reaction decreases until the battery is no longer able to provide electric energy. Most of the lead oxide and porous lead will be then in the lead sulfate form.

When the battery is to be recharged an external source of electric energy is connected to the battery terminals, but with reversed polarity in relation to them, so the reactions are reverted and the lead sulfate is electrochemically transformed into lead and lead oxide again.

The discharge-recharge process can be repeated several times with a good response of the battery, but the lead oxide plates become increasingly contaminated by lead sulfate which eventually collapsing the chemical reactions at the lead oxide plates. Besides, a sludge layer (55-60% PbSO₄; 20-25% PbO; 1-5% PbO; 1-5% metallic Pb) starts to accumulate at the bottom of the battery. Eventually, there is a moment in the battery lifetime when is no longer possible to recharge it due to the high level of contamination and, from this moment on, the battery becomes a “used battery”.

2.4. Types and Applications

Lead-acid batteries have numerous applications which may employ different voltages, sizes and weights, ranging from 2kg no-break batteries to industrial batteries which may weigh more than 2.000kg or more.

The batteries may be classified as:

- **automobile** - those batteries used as the main energy source for starting, lighting and ignition (SLI batteries) in vehicles such as cars, trucks, tractors, motorcycles, boats, planes, etc.;
- **generic** - batteries used in portable tools and devices, domestic alarm systems, emergency lights, etc.;
- **industrial** - batteries for stationary applications such as telecommunications, electrical power stations, uninterrupted power supplies or no-breaks, load leveling, alarm and security systems, general industrial use and starting of diesel motors;
- **motive** - batteries used to transport loads or people: fork lift trucks, golf carts, luggage transportation in airports, wheelchairs, electric cars, etc.;
- **special** - batteries used in specific scientific, medical or military applications, and those that are integrated in electric-electronic circuits.

2.5. Lifetime

The battery life is defined as the period of time in which a battery is able of being recharged and retain its charge. Once the battery is no longer able of being recharged or cannot retain its charge properly, its lifetime reaches its end and it becomes a “used battery” for the application it was designed for. The main cause of this “death”, as one might think that, due to the reversibility of the whole process, the battery should not have a lifetime limit, is the sulfatation process. This begins when lead sulfate (PbSO_4) precipitates over the battery plates eventually reaching a point where the ions no longer can migrate from or to the plates or electrolyte due to lead sulfate coating, and the reactions which produce the electric energy collapse.

Under ideal conditions, an automobile battery can last up to six years, but several factor contribute to decrease this optimal lifetime:

- incomplete charging process; and deep discharging process;
- battery remains too long without use or stands a long time between two charges;
- hot weather: it increases the sulfatation process;
- big energy demand: the more used, the less life time the battery will have;
- low electrolyte level: air exposed plates becomes sulfated immediately;

When all this factors are considered together, the battery life span ranges from 6 months to 48 months, yet only 30% of all batteries actually reach the 48-month mark. At this point, the battery should be considered as a hazardous wastes and, therefore, be handle accordingly in order to prevent damage to the human health or to the environment.

3. LEAD-ACID BATTERY RECYCLING – PRE-RECYCLING STEPS

3.1. Pre-Recycling Steps

Before reaching the recycle plant, used batteries must be collected, transported and stored with proper care, in order to avoid health and environmental contamination. Since these procedures are not performed inside the recycling facility, they are denominated pre-recycling steps on this document.

3.2. Collecting

The only way to implement a successful lead-acid battery recycling program is to install an appropriate and efficient lead-acid battery collection infrastructure. This infrastructure must be well planned since it involves several different sectors of the society such as scrap dealers, battery dealers, secondary lead processors and consumers into a organized scheme which provides a continuous flow of lead sources to the recycling process.

Experience has shown that, as a general trend, the most spontaneous process of used lead-acid batteries collecting occurs through the dual system of distribution-collection when manufacturers, retailers, wholesalers, service stations or other retailing points provide new batteries to users and retain the used ones to be forwarded to recycling plants. This process has its viability based on the economic value associated to the lead content in the used lead-acid batteries.

Although this collection process should be used in favor of a environmentally sound management of lead wastes, some control measures must be carried out at the collection points in order to avoid accidents that may produce human and/or environmental damage:

- batteries should not be drained at collection points:** with the exception of a few dry batteries that may arrive at the collecting point, almost all used batteries will retain its sulfuric acid electrolyte. The drainage of this liquid may pose several threats to the human health and to the environment: (a) it contains high lead levels, as soluble ions and particulate forms; (b) its acidity is very high and may cause burns and damage if accidentally spilled; (c) it requires special acid-resistant containers for storage; (d) its drainage require protected workers in order to avoid accidents, etc. Thus, battery drainage may be considered a potentially hazardous activity that demands not only special tools, containers and safety equipment but also trained personnel. Since these requirements may often be lacking, which increases the accident rate dramatically, the drainage at collection points it should be avoided;

- batteries must be stored in proper places at collection points:** the ideal place to store used lead-acid batteries is inside a acid-resistant container that may simply sealed and used as the transport container as well minimizing the accident chances. However, this is not often so and a small set of storage guidelines should be adopted:

- (a) leaking batteries, i.e. those spilling electrolyte, must be stored inside acid-resistant containers otherwise they will contaminate the environment and may cause health damage;

- (b) the storage place must be sheltered from rain and other water sources and also, if possible, away from heat sources;
- (c) the storage place must have a ground cover, preferably plastic or any other acid-resistant material, that may retain any leakage and direct it to a collecting container from where it can be removed afterwards;
- (d) the storage place must have an exhausting system, or simply a fast air renovation, in order to avoid hazardous gas accumulation;
- (e) the storage place must have a restricted access and be identified as a hazardous material storing place;
- (f) any other lead materials which may eventually arise, such as plumbing, should be conveniently package and stored in accordance with its characteristics.

Although these are general considerations, and specific problems and demands may arise within each establishment, they provide a basic set of measures that decrease the accident chances and provide a protected environment for used batteries storage.

•**collection points must not store large amounts of used batteries:** even after creating a protected storage place, a collection point should not store a large number of used batteries and must not be considered as a permanent storage place. The right storage amount depends, of course, on the trade rate of the establishment and the storage place must be dimensioned to provide enough space for a specific demand. Nevertheless, storing large amounts of used batteries, or for too much time, increase the accident chances and this must be avoided;

•**collection points must not sell their batteries to unauthorized lead smelters:** since unauthorized smelters are one of the most important sources of lead contamination, both human and environmental, it should be stressed that collection points must not sell their used batteries to establishments that do not follow high protection standards.

3.3. Transporting

Used lead-acid batteries must be considered as hazardous wastes when transport is needed. Again, the main problem in the battery transport is the electrolyte, which may leak from used batteries, requiring control measures in order to avoid accidents and specific actions to be taken in case of accident:

•**used batteries must be transported inside containers:** no matter which transport is being used, i.e. boat, train, etc., used lead-acid batteries must be transported inside sealed containers due the leakage risk, which may be high even if the batteries are appropriately transported in vertical 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 necessary to provide a shock resistant and acid resistant sealed container;

•**containers must be well packed inside the transport:** containers should not be allowed to move while being transported. Therefore, they must be tied up or pile up properly to avoid this problem;

- the transport should be identified with symbols:** the transport must be correctly identified, following international conventions, symbols and colors, meaning that corrosive and hazardous products are being transported;
- specific equipment:** a minimum set of equipment necessary to combat any simple accident should be provided and the transport team trained on how to use it;
- drivers and auxiliaries should be trained:** people dealing with hazardous wastes should always be trained in emergency procedures, including fire, spilling, etc. and by which means the emergency response staff could be contacted. Besides, they should be aware of the specific kind of hazardous material is being transported and how to deal with it;
- individual protection equipment:** IPE should be provided for the transport team in order, and also training on how to use the equipment, in case of any accident;
- transport schedule and map:** if possible, hazardous waste transport should always predict possible accidents or other specific problems. This is made possible if they follow a certain predefined path and restricted to a known schedule.

The points above mentioned are not an extensive list. Much more specific trainings and instructions could and, in fact, should be provided to transport teams, since the transport may involve, or pass through, heavily urbanized areas or other sensitive locations that could be strongly affected by accidents.

3.4. Storing

After being transported, the batteries should be now arriving at the recycling plant. Although some protection measures are very similar to the storage procedures at the collection points, the striking difference between them is the amount of batteries that must be stored at these facilities, easily reaching several thousands of tons. Therefore, a different approach should be adopted here:

- batteries should be drained and prepared for recycling:** better recycling rates and less environmental problems are created by recycling drained batteries. Therefore, they should be drained, the electrolyte directed to treatment station and the batteries stored empty and ready to be recycled;
- batteries should be identified and segregated:** different batteries may require different recycling approaches. Therefore, they should be correctly identified, labeled and stored in different places;
- batteries must be stored in a proper hangar or covered place:** unless some specific circumstances require it, container storage is no longer practical at the recycling plant, since batteries should be now classified, identified and carefully segregated. Therefore, a proper hangar, or in the worst case a covered place, should be constructed to store them and must have a minimum set of characteristics:
 - (a) it must have an impermeable and acid-resistant floor;
 - (b) it must have an efficient water collection system which directs spilled solutions toward the effluent or acid electrolyte treatment station;
 - (c) it should have only one entrance, which should stay closed unless otherwise necessary, in order to avoid dust release;

- (d)** it should have a special gas collection system, which filters the air to remove lead dusts and at the same time renews the air inside the hangar;
- (e)** it must be provided a proper fire combat equipment. Although it is unlikely to happen a fire due to the batteries themselves, it must be thought that accidents by other causes could set fire on the batteries due to their high content of carbon. Therefore, fire combat equipment is necessary;
- (f)** only authorized personnel should be allowed to enter the hangar.

Again, these are just general consideration that must be adapted for the specific requirements of each recycling plant. More restrictive and careful approaches are encouraged.

4. LEAD-ACID BATTERY RECYCLING

The pre-recycling steps finish when the batteries are received and properly stored at the storage place in the recycling plant. After this, the used batteries enter into the recycling process which could ideally be divided in three major processes:

- (a) battery opening or breakage;
- (b) lead reduction;
- (c) lead refinement;

4.1. Battery Opening

No matter the recycling technology to be adopted, batteries must always be drained before they are inserted in the recycling process, since the acidic electrolyte produces several complications in the lead fusion-reduction. After drainage, batteries may or may not be broken, depending on the specific recycling process adopted.

Classic methodologies of lead recycling processes, including Water-Jacket, reverberate ovens, electric ovens, and short and long rotating ovens, do not require battery breakage before the smelting process. The drained batteries are inserted directly in the recycling process since pyrometallurgical techniques accept organic materials and other substances, which are burned or incorporated into the slag formation.

However, if a new plant is to be build up, processes in which the batteries are broken prior to the recycling process are preferable due to:

- (a) increase in the lead production and decrease in the slag formation;
- (b) possibility of soft lead production as well as antimonial lead;
- (c) possibility of polypropylene recovery;
- (d) simplification of furnace smoke treatment;
- (e) pyrometallurgical techniques cannot accept the acid from battery electrolyte;

Furthermore, improvements in the battery production industry lead ultimately to the production of sealed batteries and other systems which are no longer easily drained. Therefore, an increasing amount of batteries must be broken before entering in the recycling process.

4.1.1. Historical Background of Battery Opening

Before the 1960 decade, batteries were opened mainly by ax just when the recycling process demanded a lower organic content into the furnace otherwise they were inserted directly into the furnace. Although this situation has changed in most countries, specially in the developed ones, unfortunately it has not in most developing countries. It must be stressed, however, that manual opening of batteries should be avoided at all costs, not only because it is a major source of human

health contamination but also because it is an environmental unsound management of these wastes. Nevertheless, some modern smelting plants still require manual opening of big industrial batteries that cannot be broken in normal apparatus due to its size. If such technique is needed, all proper measures must be taken to provide protection to the workers and the environment.

During the 1960 and 1970 decades, the battery opening evolved to a mechanical guillotine or saw that greatly reduced the human contact with the breakage process. They were also incremented with automatic feed and were the first examples of entirely mechanized systems, some of them still in use.

From 1980 on, most of the modern smelting plants were adopting a totally mechanized system in which the batteries were received, transported and broken into sufficiently small pieces in order to separate the battery constituents:

4.1.2. Modern Battery Opening

The modern battery opening process (figure 2) starts with the arrival of used batteries at the recycling facility. Human contact is usually minimized as much as possible so the used batteries are received and directed to the opening apparatus by means of automatic mats or small wagons whenever possible.

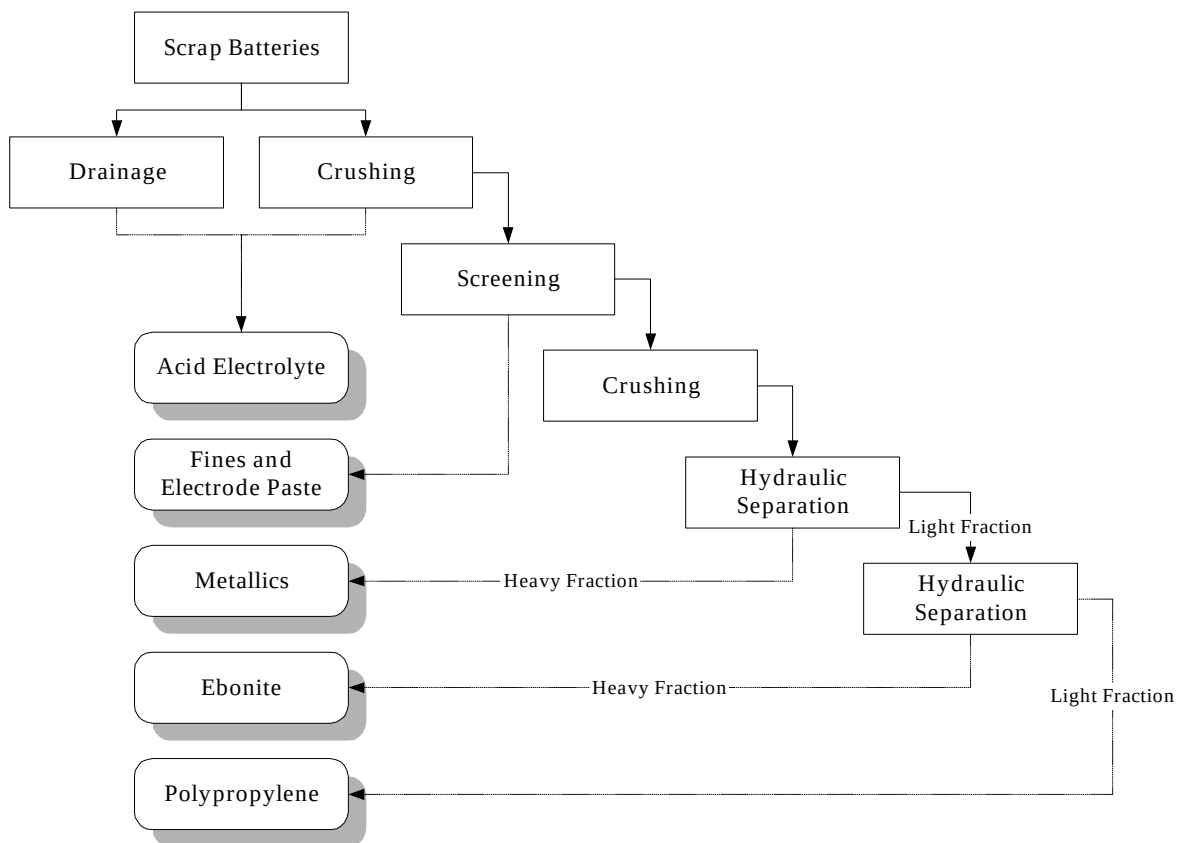


Figure 2: battery opening process.

Once the batteries arrive at the opening machine, they are processed in hammer mills, or other crushing mechanisms, that break them in small pieces. This breakage procedure ensures that all components, such as lead plates, connectors, plastic boxes and acid electrolyte are easily separated in the subsequent steps.

After breakage, the lead oxides and sulfates are separated from the other materials through sieving and filtering, either under water flow or dry, since they are usually crushed to a fine granulometry. After separation, they are directed to the oven, in case of pyrometallurgic techniques, or other processes, in the case of hydrometallurgical techniques.

After the first rough breakage, sometimes there are other crushing mechanisms that further decrease the granulometry of the remaining materials. The metallic parts, including lead plates, grids, connectors and bornes, are then separated from the organic parts, which include boxes, either PVC or ebonite, PVC plate separators, etc., by means of density difference in hydraulic separators which differ from process to process.

Other processes, through use of density properties and hydraulic mechanisms, separate the broken battery pieces in three different layers: the first one is constituted of light fractions such as plastics, the second is constituted of fine granulometry pieces of lead oxide and sulfates and the third one is the heavy layer constituted of lead plates, connectors, etc.. This method, therefore, lacks the filtration step in order to remove lead compounds prior to plastic recovery. However, the complexity of these systems make them difficult to regulate and use.

After these separation steps, the organic layer is further separated into polypropylene wastes (called light organics), and separators and ebonite (called heavy organics). The light organics are then milled to small pieces, according to their future use, while the ebonite and separators are conveniently stored. Unless the breakage system is connected to the oven in a continuous process, the lead compounds and metallic parts are also stored until further processing.

Battery opening methods differ from one another in process details and evolve as new technology becomes available. The suitability of each one for a given lead recovery plant depends on several specific factors such as local economy, quantity of raw materials as well as the demands of the smelting facility. Some examples of these systems are the Metaleurop, Bunker Hill, Engitec and MA Engineering, which can be understood in detail by consulting specialized references.

4.1.3. Battery Opening: Potential Sources of Environmental Contamination

This section, and the other two sections in the lead reduction and lead refining processes, were not designed to describe or extensively list all possible sources of contamination that may occur in the lead recovery processes, since this is an impossible task. They were designed, instead, to list just a short and predictable list of common contamination sources and where to look at when searching for them. Specific sources of contamination will have to be determined under the light of the employed process. Methods of contamination prevention will be treated in the environmental protection chapter. That stated, the common sources of environmental impacts in the battery opening 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 injury since the electrolyte is not only a strongly corrosive solution but also a good carrier for soluble lead and lead particulate. 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 particulate once the solution dries out and the lead becomes incorporated into soil particles which may be blown by wind or raised by vehicle transit;

(b) manual battery opening – source of human health injury and environment damage through heavy spillage and lead contaminated dust formation: manual opening 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 human health damage. Therefore, it should be avoided at all costs;

(c) mechanical battery opening – source of lead particulate: the process of opening batteries through crushing on hammer mills may spread lead particulate. However, the use of water flow inside the mill prevents the formation of such particulates;

(d) hydraulic separations – contaminated water leakage: the hydraulic separations, both metallic from organic and heavy organics from light organics, are usually performed inside sealed machines and with a closed water system. However, if any water leakage occurs, it will be heavily contaminated by lead compounds;

(e) ebonite scraps – contaminated wastes: ebonite scraps removed from the opening process may pose a problem, since they are usually contaminated by levels as high as 5% (w/w) of lead. Therefore, it must be planned in advance its proper destination and control of possible hazards, both human and environmental, coming from this source.

4.2. Lead Reduction

The battery scrap obtained from the opening process are in fact a mixture of several substances: metallic lead, lead oxide (PbO), lead sulfate (PbSO₄) and other metals such as calcium (Ca), copper (Cu), silver (Ag), antimony (Sb), arsenic (As) and tin (Sn). In order to isolate the metallic lead from this mixture, two methods may be applied: pyrometallurgical methods, also known as fusion-reduction methods, and hydrometallurgical methods, or electrolytic methods.

4.2.1. Pyrometallurgical Methods

The objective of the pyrometallurgical methods, or fusion-reduction methods, is to chemically reduce all metallic compounds to their metallic, or reduced, forms by means of heating and providing adequate trapping and reducing substances (figure 3).

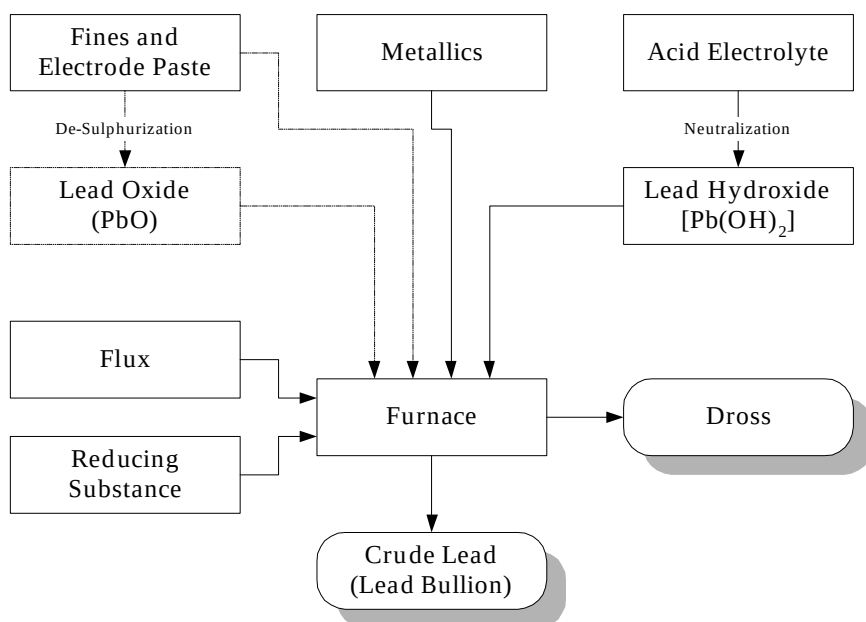


Figure 3: diagram of a smelting lead process

Prior to smelting, some methods may de-sulphurise the lead sulfate paste by reacting it with a mixture of sodium carbonate (Na_2CO_3) and sodium hydroxide (NaOH), such as in the CX and related processes, converting the lead sulfate (PbSO_4) in lead oxide (PbO). Sometimes the de-sulphurizing agent may also be iron oxide (Fe_2O_3) and limestone (CaCO_3). This procedure reduces the amount of slag formation and also, depending on the smelting method, the amount of sulfur dioxide (SO_2) released to the air. However, other methods simply add controlled amounts of lead sulfate as well as de-sulphurizing agent directly in the furnace.

The acid electrolyte must also be treated before being sent to the smelting furnace. This is carried out by neutralization of the electrolyte solution with sodium hydroxide, which precipitates all present lead as lead hydroxide $[\text{Pb}(\text{OH})_2]$. This compound is then removed by decantation or filtration and directed to the furnace. The remaining solution, a sodium sulfate diluted in water (Na_2SO_4), may be further purified and the salt isolated in high purity grades, such as in the CX Engitec Impianti process.

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.. There are also several different vessels in which the smelting process may be carried out: rotatory furnace, reverberatory furnace and blast or electric furnace, rotary kiln, etc. The best method depends, again, on several factors that include local economics, planned amount of recycling, etc. and specific information may be found on the references provided at the end of this guideline.

The fluxing agents, which melt at a temperature below the lead smelting temperature, are added not only to decrease the lead smelting temperature but also to provide a liquid solvent which traps several unwanted compounds while the smelting and reducing processes undergoes. 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 its later treatment, are entirely dependent on the chemical composition of the flux that was used.

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

The quantity of flux and reductant added must be carefully controlled:

- (a) an insufficient amount of flux will not trap all sulfur and other materials present in the scrap and a great quantity of sulfur oxides may be released;
- (b) an insufficient amount of reducing agent, on the other hand, will not reduce all lead oxides present in the scrap and the slag will be highly contaminated with lead, which may be a potential source of environmental hazard.

After the process had been properly balanced, the melted metallic lead starts to accumulate in the bottom of the kettle. 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.

4.2.2. Hydrometallurgical Methods

The objective of the hydrometallurgical methods, or electrolytic methods, is to electrically and selectively reduce all lead compounds to metallic lead, such as in the PLACID technology (figure 4).

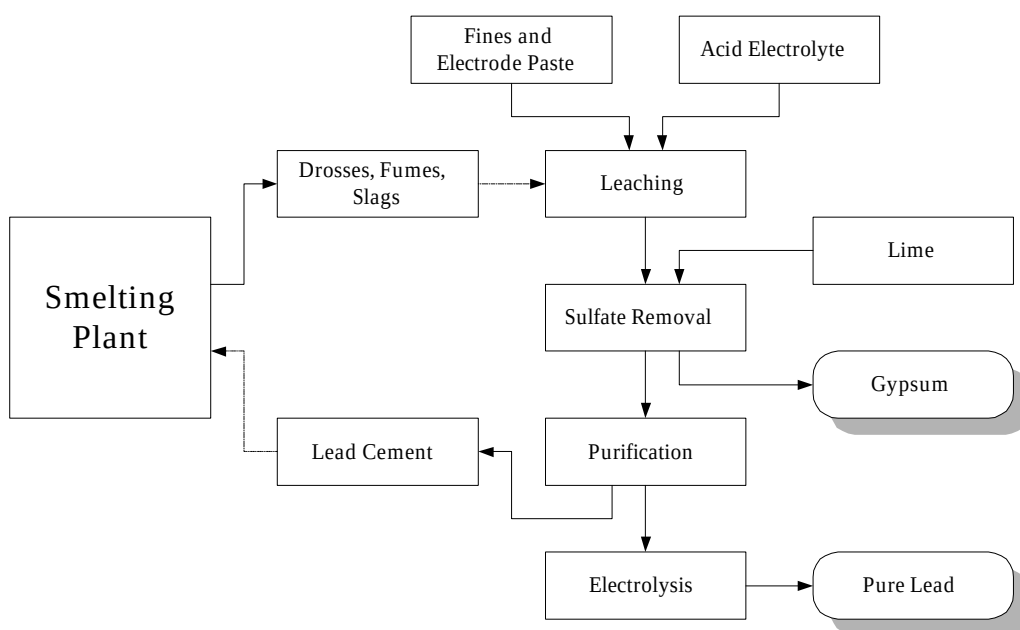


Figure 4: diagram of a electrolytic lead process

Although it may be sometimes costly when considered as an isolated plant, this process provide good results when linked to a smelting plant since, with the appropriate separation of raw materials, it is a technological solution to the lead refining processes.

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^{2+} or plumbous lead) in this case, which is then electrolytically reduced to produce metallic lead (figure 5).

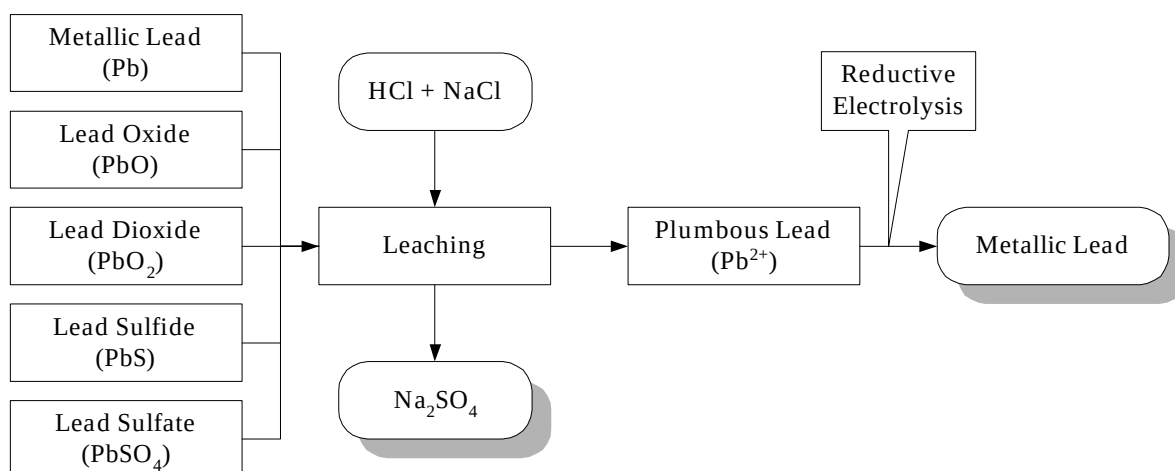


Figure 5: electrochemical process in hydrometallurgical lead production.

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, which can then be conveyed to a kettle for casting into ingots. The whole extraction process can be run continuously 24 h/d, without interruption.

4.2.3. Lead Reduction: Potential Sources of Environmental Contamination

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

- (a) lead compounds derived from the opening process – *lead and lead compounds in dust and water*: the separated and fine materials from the opening 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 opening 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 powder and may contaminate the factory and its surroundings as normal 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 inlet but, since they are usually in powder form, they may be a source of lead dust while being transported;
- (c) filters – *lead contaminated dusts*: ovens do need filters in order to capture lead dusts formed in the fusion kettle. After being used, they are usually recycled in the same fusion process since they may contains as much as 65% of lead. However, the handling of these used filters may be an important source of contaminated dust, which may pose threats 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 oven inlet is itself a source of lead dust to the environment, since it is an opening system. The high temperature smokes that leave the oven inlet and ingot producing system, for example, have a high lead content, and is readily absorbed by the human body;
- (d) sulfur dioxide (SO₂) emissions – the percentage of sulfur from a given amount of lead scrap load that leaves the reduction system as sulfur dioxide (SO₂) is highly dependent not only on the oven

itself but also in the kind of skim material being formed. As a general trend, this number may fall between 0% to 10% and it is significantly reduced if the flux used is a sodium based compound producing sodium skims. Ebonite also has 6-10% of sulfur that may contribute to the SO₂ emission if it is added to the oven;

(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 becomes the reduction process, the greater are the tar emissions, specially in artisanal foundries. If the reduction oven has filters, the emission of tars is an even greater problem since they are very pyrogenic and may produce fires in the filters, thus increasing the accident chances. The introduction of afterburners to complete the combustion of gases from the oven are an usual solution to this problem, but a complete restructuring of the process, removal of organics for example, may present better perspectives;

(f) chlorine (Cl₂) and chlorine compounds emission: an initial separation of the materials allowed to enter the reduction process reduces the chlorine emission considerably. However, increasing amounts of PVC in the oven 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 in the oven conditions but captured by dust filters as the temperature decreases;

(g) scoria production: this is the majority of the waste production during the reduction process. As an average picture, around 300-350kg of scoria are produced for each ton of metallic lead, depending on specific factors of the process and the kind of scoria being formed (calcium or sodium skims), and around 5% (w/w) of this scoria are lead compounds. Therefore, specially considering the leach that may be produced if the scoria enters in contact with water or moist, a proper destination and storage place to this material must be planned well in advance in order to avoid human health and environmental problems.

4.3. Lead Refining

As early indicated, if a smelting plant stops at the stage of the fusion-reduction plant, it will produce what is known as hard or antimonial lead. If the plant is meant to produce soft lead, the crude lead must undergo a refining process. The objective of the refining process is to remove almost all copper (Cu), antimony (Sb), arsenic (As) and tin (Sn), since soft lead are not allowed to have more than 10g per ton of these metals.

There are two methods of lead refining: hydrometallurgical methods, which were already described in the lead reduction section, and pyrometallurgical or thermal processes, which are described here.

4.3.1. Pyrometallurgical Refining

Thermal refining is performed in liquid phase, which means that the crude lead must be melted to temperatures from 327°C (lead fusion point) to 650°C (lead boiling point). As a general trend, the process is performed in batches of 20 to 200 tons, according to the refining plant capacity.

The chemical concept behind the refining process is the addition of specific reagents to the molten lead at proper temperatures. These reagents will then remove the unwanted metals in a specific order as they are added selectively (figure 6).

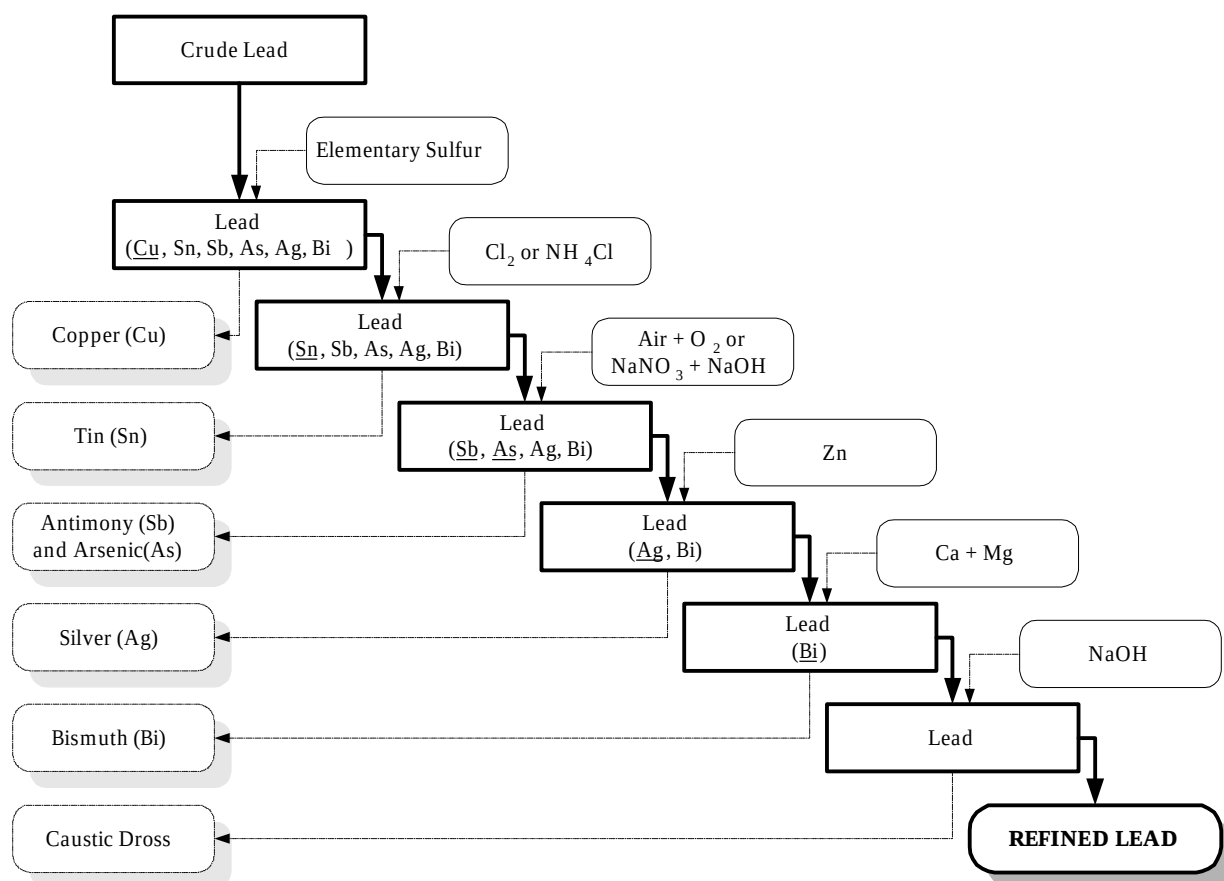


Figure 6: pyrometallurgical lead refining.

Copper (Cu) is the first element to be removed with elementary sulfur in a two phase procedure. In the first step, almost all copper is removed as a copper sulfide (CuS) skims when elementary sulfur is added to the molten lead at 450°C. The second step is meant to remove all remaining copper by adding small amounts of elementary sulfur to the molten lead at 330°C until no reaction takes place anymore.

Tin (Sn) is next removed BY either chlorine (Cl₂) or ammonium chloride (NH₄Cl) oxidation. The addition of chlorine to the molten lead at 500°C produces tin chloride (SnCl₂) skims which are mechanically removed. Although this is the current method for tin removal, its inconvenient is the parallel removal of small amounts of antimony (Sb) and arsenic (As) by oxidation.

Arsenic (As) and antimony (Sb) are selectively removed by oxidation with either air enriched with oxygen (O₂) or a mixture of sodium nitrate (NaNO₃) and sodium hydroxide (NaOH). The temperature of the molten lead is raised to 550°C and a flow of O₂ enriched air is bubbled into it. The reaction is extremely exothermic and the temperature easily reaches 650°C. Them skims are a mixture of oxides (25% Sb, 10% As and 65% Pb).

Silver (Ag) come next and its removal is carried out by the Parkes Process, which makes use of the preferential solubility of silver in molten zinc (Zn) instead of molten lead (Pb). Therefore, metallic zinc (Zn) is added to the molten lead at 470°C and the mix is allowed to cool to 325°C. A silver-lead-zinc alloy separates and forms a crust on the surface. The crust is removed and the zinc separated from the silver by vacuum distillation. The crude silver is further refined using oxygen to produce fine silver. The excess of zinc is removed from the de-silvered lead by vacuum distillation and then by sodium hydroxide (NaOH).

Finally, bismuth (Bi) is removed by treatment of the resulting lead with a mixture of calcium (Ca) and magnesium (Mg), also known as the Kroll-Betterton process. A calcium-magnesium-bismuth alloy is formed as dross on the surface of the molten lead and then removed by skimming. The skims are oxidized and further refined to produce fine bismuth.

The pure lead is then treated with sodium hydroxide (NaOH) to remove any left impurities and finally cast into blocks or ingots. Fumes, drosses, litharges and other substances formed during the refining process are usually smelted in a small blast furnace to produce crude lead which is reintroduced in the refining circuit.

4.3.2. Lead Refining: Potential Sources of Environmental Contamination

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

- (a) over heated lead – *lead steams*: 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 vapor;
- (b) sulfur dioxide (SO₂) emissions: the copper removal by addition of elementary sulfur may produce large quantities of sulfur dioxide (SO₂), since sulfur oxidizes readily in the presence of oxygen at the oven temperatures;
- (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. Usually in the form of a very fine and dry dust with several percent of lead and other metals, it may be hard to provide adequate transport, storage and sound destination to this hazard material;
- (d) chlorine (Cl₂) tin (Sn) removal – *chlorine gas release*: the tin removal by chlorine gas 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 (O₂) enriched air tin (Sn) removal – *lead steam*: while the air is being passed inside the molten metals, the nitrogen (N₂) 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 steams;

5. ENVIRONMENTAL CONTROL

Up to this point several aspects of lead recycling have already been described, including collecting, handling, storing, transporting, opening batteries, lead reduction and refining. Nevertheless, some important issues remain to be discussed, specially concerning environmental control measures.

The environmental control process may be divided in three main subjects according to the degree on implementation of the recycling plant: (a) the recycling plant have not yet been implemented; (b) the recycling plant was constructed in the past and needs technological improvements and monitoring

guidance; and (c) the recycling plant follows the best available technologies and only needs monitoring guidance.

5.1. Lead Recycling Plant Planning – Environmental Impact Assessment (EIA)

The Environmental Impact Assessment (EIA) is a study performed before the implementation of any possible pollution source and its objective is to evaluate the environmental consequences of the implementation of an industrial project during its conception phase. This study provides, therefore, elements for the project improvement and also data to guide decision-makers, investors and governments and make them aware of the project consequences. The EIA studies are usually mandatory in several countries around the world and the project implementation investments are just released after the study has been presented to and approved by the governmental agencies.

Theoretically, this is the step through which every lead-recycling facility should undergo in order to prevent environmental pollution and provide every aspect of environmental and human health protection. It is also the step which provides the best chances to make changes in the project at minimum costs and also to plan ahead in terms of best available technologies for a chosen recycling technique. Finally, it provides guidance on how the recycling plant relates to its surroundings, not only in environmental terms but also economically, socially, etc..

An EIA should include the sections described below, and a more complete guide for an EIA may be seen in Annex I:

- (a)** targets and objectives of the project as well as its social and economic importance;
- (b)** description of the implementation site, the project itself and the relation between them both, including the maximum available quantitative elements;
- (c)** a chronogram of activities;
- (d)** quali-quantitative identification of the environmental impacts and actions that will be employed to diminish these impacts as much as possible;
- (e)** possible measures to rehabilitate the site after or if the project ends;
- (f)** applicable laws in relation to the project;
- (g)** alternatives to the project implementation, specially alternative sites;
- (h)** dimensions, technologies employed, raw material sources, energy sources and products;
- (i)** justification for the employed methods and technologies;
- (h)** finally, the EIA must be a concise and objective report, and value judgments must be avoided as much as possible.

Despite its obvious utility, sometimes the EIA becomes a small drawback because: (a) the EIA is not always made public; (b) it may be considered as an end and not as a part of a major context of environmental management; (c) it is usually produced by independent partners and not necessarily reflects the commitments of the corporation which requested the study; and (d) it may be employed as a source of excessive requirements and constrains thus providing means of market control.

5.2. Technological Improvements

If an EIA was not performed before the implementation of a lead recycling plant, it is mostly probable that the facility has some technological and environmental problems to solve, since some important steps were missed or overlooked. However, it must be stressed that simply closing a lead recycling plant that is not working so well and building a brand new one is not always the best solution, since this action requires a huge amount of money. Therefore, the implementation of technological improvements and the seek of environmental monitoring may be the best available option, and perhaps the only one. Technological improvements will be described in this section while environmental monitoring will be treated in the next one.

5.2.1. *Pollution Sources Treatment and Pollution Prevention*

In a modern lead recycling plant, the cost of pollution treatment, including effluents, smokes and dusts, and elimination of sulfur dioxide (SO₂), amount 20-30% of the investment costs.

5.2.1.1. Acid Electrolyte and Effluents

The direct elimination of these liquids in the environment without treatment consist in a huge source of environmental impacts. A suggested approach to the problem is trying to valorize them as much as possible in accordance with the available budget:

- (a)** there are some technologies used to remove, by liquid-liquid extraction, the sulfuric acid present in the electrolyte. These technologies provide means to produce lead-free acid, which can be used as electrolyte again or sold;
- (b)** the electrolyte may be treated by sodium carbonate (Na₂CO₃) or calcium carbonate (CaCO₃), thus producing sodium sulfate (Na₂SO₄) or gypsum (CaSO₄) which, after removing lead sludges by filtration, can be further purified and sold;
- (c)** direct discharge of neutralized electrolyte should be avoided as much as possible;
- (d)** discharge of untreated electrolyte is not environmentally sound and must be avoided at all costs.

Besides, every lead recycling plant should have an effluent treatment station in order to treat the water that must leave the recycling facility, including those coming from the electrolyte neutralization, rain water, spilled water from battery storage, etc., in order to control, protect and improve the water quality.

5.2.1.2. Dust Collection and Air Filtration

All steps in the battery recycling plant release some sort of smoke or dust, which must be collected and treated before being released to the environment. Considering that an average recycling plant must filter around seventy tons of air for each ton of produced lead, it becomes clear that this is an important process to control.

The so called “mechanical” dust, i.e. particulate material with large physical characteristics, are relatively easy to filter and remove from air. However, the finer the dust, the difficult to remove it and special techniques must be employed in order to clean the air. There is a wide range of options

that must be judged as a function of contamination level requirements and budget: fabric or bag filters, electrostatic precipitators, wet electrostatic precipitators, cyclones, ceramic filters and wet scrubbers. As a general trend, all collected dusts are directed toward the smelting plant in order to collect the lead.

5.2.1.3. Sulfur Dioxide (SO₂) Elimination

Some countries have very restrictive sulfur dioxide (SO₂) emission parameters and, in fact, this is an important pollutant to control since it produces severe impacts on the environment. Its elimination may be carried out in several ways, such as dry, semi-dry, semi-humid and humid processes, and a simple alternative is the use of wet scrubbers with calcium carbonate (CaCO₃) as reagent, which produces sulfurous gypsum. This compound can be, in turn, sold or used in the oven as scoria formation reagent. Even after filtration and removal of dust, however, the gases will still have vestigial dust and SO₂.

5.2.1.4. Use of Oxygen (O₂)

Oxygen (O₂) is used to enrich the air that is used in the heating processes and it has three main consequences:

- (a)** since air has a big percentage of nitrogen [N₂, ~72% (v/v)] which does not participate in any chemical reaction at normal temperatures, the use of pure oxygen (O₂) decreases dramatically the amount of combustion gas formation (around five times);
- (b)** decrease in heat loss, since less cold gas is flowing through the oven;
- (c)** increase in the oven production;

Therefore, the use of pure oxygen (O₂) provides a much cleaner production.

5.2.1.5. Flux Agent Choices and Scoria Valorization

Calcium scoria, formed by the addition of calcium carbonate (CaCO₃) flux to the oven, at the same time that produces a less lixiviable slag, which means a more environmentally sound waste, it increases the working temperature of the oven and releases more sulfur dioxide (SO₂), which means more energy costs and alterations in the oven performance. On the other hand, limestone (CaCO₃) is a natural product that is much easier to deal with than sodium carbonate (Na₂CO₃), decreasing flux costs and other operation problems. Therefore, the choice of the fluxing agent must be well planned.

Valorizing the scoria, which ultimately means controlling the fusion-reduction-refining steps very well, would be a huge step toward cleaner production, since this is the major waste formation in the whole process. The sodium scoria, arising from the utilization of sodium carbonate (Na₂CO₃), does not have any use due to its physical and chemical properties, and, therefore, it is being directed to hazardous waste landfills.

On the other hand, despite some cost increases in the recycling, the calcium scoria have found some use as a raw material in the concrete production which has been employed in road building, bricks, etc., with promising results. Therefore, the utilization of calcium based flux may be considered as a viable option in the future since it provides a solution to a great amount of wastes.

5.2.1.6. Heavy Organics Recycling

The heavy organic fraction is constituted 50% by plate separators and 50% by ebonite, and 50% of its mass is carbon which means the heavy organics may be used as a reducing agent in the oven. Despite the fact that some extra care must be taken in order to prevent pollution, the usage of heavy organics as reducing agent decreases the amount of other reducing agents and also decreases the amount of wastes that otherwise would require a sound management. However, some process drawbacks, such as less fluid scoria, tar formation and others, did not led to a conclusive report and further studies are required, but this is a promising destination for these wastes.

5.2.1.7. Polypropylene Recycling

Polypropylene is such a valuable product that it alone could sustain the lead-acid battery opening. Therefore, processes of plastic separation and recycling should be seen as a profitable activity that, unfortunately, are not much spread worldwide.

5.2.1.8. Sound Destination to Unrecoverable Wastes

Some wastes produced during the lead recycling process will no be further recyclable or reusable and, therefore, will need a sound destination. 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 lixiviable, and thus require a destination in a hazardous waste landfill.

5.3. Environmental Monitoring

Cleaner technologies require permanent monitoring, even after implementing the best available technologies. This process not only provides a clear picture of the lead recycling plant environmental performance, since it correctly identifies the defective steps in the recycling chain, but it also provides concrete data in order to improve the process, and increase the degree of environmental and human health protection. Ultimately, the environmental monitoring keeps the environmental soundness of the recycling process.

On the other hand, control measures ensure that procedure mistakes and accidents are decreased as much as possible, also providing a simple set of instructions that, if followed, decrease significantly the risk of environmental contamination.

5.3.1. Control Measures

Independently of the pollution combat technologies employed at the recycling plant, some miscellaneous control measures are widely adopted in order to prevent or minimize environmental contamination. The actions below described are just a small set of these measures and further improvements, identified by pinpointing and dealing with specific characteristics of each recycling plant, are encouraged. However short, the list provides some useful ideas in achieving good environmental control practices.

- individual protection equipment:** all workers must have their own IPE, which are different for each section of the recycling plant, depending on their specific requirements. They must also be trained on how to use them and all sections of the recycling plant should have clear and visible

identification of what IPE a worker should be using while in that specific sector. The minimum IPE requirements would be respirators;

•**work practices:** some working policies should be adopted and the workers trained to follow them, in order to decrease the health contamination risks:

- (a) prohibit smoking in the working place;
- (b) segregate the work and eating areas;
- (c) enforce showering at the end of work;
- (d) change out of work clothes before going home;
- (e) change and launder workwear daily;
- (f) check and clean respirators daily.

•**opening, reduction and refining operations inside enclosed buildings:** allowing the collection of all dusts through a convenient filtering system and avoiding the release of contaminated dusts to the atmosphere;

•**non covered areas:** all non covered areas of the recycling plant should be of a hard and smooth surface, preferably paved with impermeable material, easily swept. All swept materials should be collected and directed toward the reduction furnace in order to recycle possible lead and other metal dusts;

•**internal transports should be enclosed conveyers:** avoiding the releasing of unnecessary dusts. When this is not possible, the transport container should be properly covered. Internal transports should be segregated from external vehicles;

•**scoria storage:** hazardous materials should be storage with the same degree of care that used batteries, since they contain many hazardous materials and substances that may leach or produce other health and environmental problems. Therefore, the same control measures adopted to battery storage (paved soil, covering, etc.) apply to slags, scoria, skims and other hazardous wastes and materials;

•**air filtering system:** it should be as close as possible of the exhausting area and all recycling systems should be a closed system to avoid dust release;

•**all open operations should be wet:** wetting avoids dust formation. Therefore, all operations outside enclosed buildings, such as sweeping, road cleaning, transport over unpaved roads, open container transport, baghouse fume and dust removal, dust transport, etc. should be performed with wet materials;

•**trucks and transports should be washed when leaving the recycling plant:** specially wheels and lower parts, avoiding the spread of lead dusts outside the recycling plant. Inside of cabinets should be vacuum cleaned once in a while. All vehicles should leave the recycling plant through only one controlled exit;

•**coal storages should be protected:** if the recycling plant uses coal, either as a fuel source or as reductant, it should be properly stored in a insulated and covered area. It also requires special fire combat equipment and trained personnel;

•**rainwater must be collected:** since it can produce hazardous leachates, a specially designed water collecting system should be adopted in order to direct all waters to the effluent treatment station;

Independently of the pollution combat technologies employed in the recycling plant, some miscellaneous control measures are widely adopted in order to prevent or minimize environmental contamination. The actions described below are just a small set of these measures and further improvements, identified by pinpointing and dealing with specific characteristics of each recycling plant, are encouraged. Nevertheless, the list provides some useful ideas in achieving good environmental control practices.

5.3.2. Monitoring Measures

Environmental monitoring may be thought as an environmental contamination thermometer. The data collected through it may be used not only as a guide to technological improvement and performance measure, but also as a source of credibility and trustfulness in the relationship with the surrounding population, since lead recycling plants are usually seen as a huge source of environmental contamination. Therefore, it should be done by every lead recycling plant.

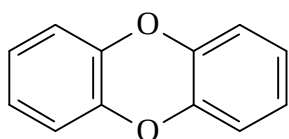
Some monitoring targets are:

- effluents:** after being treated at the effluent treatment station, every water leaving the recycling plant should be monitored in order to determinate, at least, its pH, sulfide content and representative heavy metals (Pb, Hg, and Cd);
- gases:** there must have a continuous monitoring of gases such as sulfur dioxide (SO₂) and lead dusts. It is desirable that this monitoring should be performed at several different points inside and outside the recycling plant;
- soil and plant:** periodical analysis of soils and plants inside the recycling facility and in the immediate surroundings should be performed in order to detect the dust contamination;
- air quality:** there must have a continuous monitoring of the air quality inside the enclosed buildings such as in the battery opening facility, etc.;
- medical surveillance:** all workers must be health monitored and a record must be kept. Immediate surrounding population should also be checked periodically;

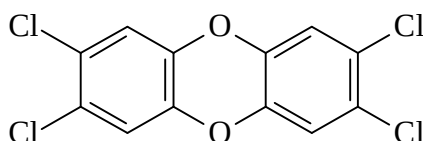
Although these monitoring activities are costly and several of them need specialized personnel, which may be constitute a major problem when budget constrains are an important factor, it must be realized that they provide data of utmost importance in order to determine the environmental soundness of the recycling plant. They should, therefore, be pursued whenever possible.

5.3.3. Dioxins

Dioxins are aromatic organic compounds that may be formed by a thermal reactions, denominated *de-novo* process, in which precursor fragments, usually highly reactive molecules, react with each other yielding dioxin molecular skeletons (figure 7).



Dibenzo-*p*-dioxin



2,3,7,8-Tetrachloro-dibenzo-*p*-dioxin

Figure 7: dioxin skeleton and 2,3,7,8-TDD.

The presence of chlorine atoms in the precursors seems to increase the rating of dioxin formation and yields much more hazardous molecules, such as the 2,3,7,8-TDD, a potent carcinogenic compound.

Despite the difficulty of addressing and detecting dioxin formation, it is a relevant subject to the lead recycling process, since secondary raw materials may contain dioxin precursors and the furnace environment may provide good dioxin formation conditions. Also, the use of carbon reducing agents and organic fuels may produce fine carbon powder that, under specific conditions, may react with chlorine derivatives and produce toxic compounds. Finally, the presence of copper and iron, both commonly found in lead recycling processes, seems to catalyze the dioxin formation to a certain extent, which would further increase the dioxin generation.

Since pre-selection of the raw materials in order to remove chlorinated organics and metals such as iron and copper seems to be an improbable, if not impossible, task in a lead recycling plant, with the exception of light and heavy organics, dioxin destruction must be the easiest approach to the problem:

- oxygen (O₂) enriched air or pure oxygen can be used to ensure complete combustion of organic compounds, as already mentioned, and it could, in principle, decrease substantially the dioxin formation;
- activated carbon can be injected into the gas stream in order to absorb the organic molecules and, afterwards, be filtered. The dust must be treated as hazardous and must not be directed to the furnaces, but instead incinerated in specialized facilities or treated with extreme careful;
- catalytic oxidation has been reported as an efficient method for dioxin destruction.

These and other available technique must all be considered according to the specific constrains and requirements of each recycling plant. Several of them do not require special facilities and can be easily incorporated into the process without further improvements. The most cost effective system will also depend on safety, legal and operational aspects as well as economic factors. Emission levels below 0.5ng per cubic meter can be achieved by using any of the above techniques and, through a combination of techniques, it is not hard to achieve levels below 0.1ng per cubic meter, which would be enough for health and environmental protection.

6. HEALTH ASPECTS

6.1. General Considerations

Lead is, and always has been, naturally present and quite abundant not only in the environment and but also in man. Natural mobilization of lead occurs by weathering of mineral deposits and gaseous emissions and it has been estimated that, together, these two mechanisms release about 210.000 tones of lead into the environment each year and were, until the appearance of human activities, the only source of environmental lead. The average concentration of lead in the lithosphere is about 16 mg/kg but this value changes in relation with the specific composition of the local minerals.

In comparison with the naturally mobilized quantities, human activities release lead from its natural sources much more intensely, amounting more than 4 million tones/year, yet just a small fraction of this returns to the environment as a contamination source whereas the major part enter of it is directed to industrial processes.

Since the human body does not discriminates from where the lead is coming from, i.e. anthropogenic lead and natural lead are absorbed in the same way, all human activities that inadvertently release lead in one form or another into the environment may be considered as a magnifier of the natural source, but the major sources does not change themselves and may be depicted as in the figure 8.

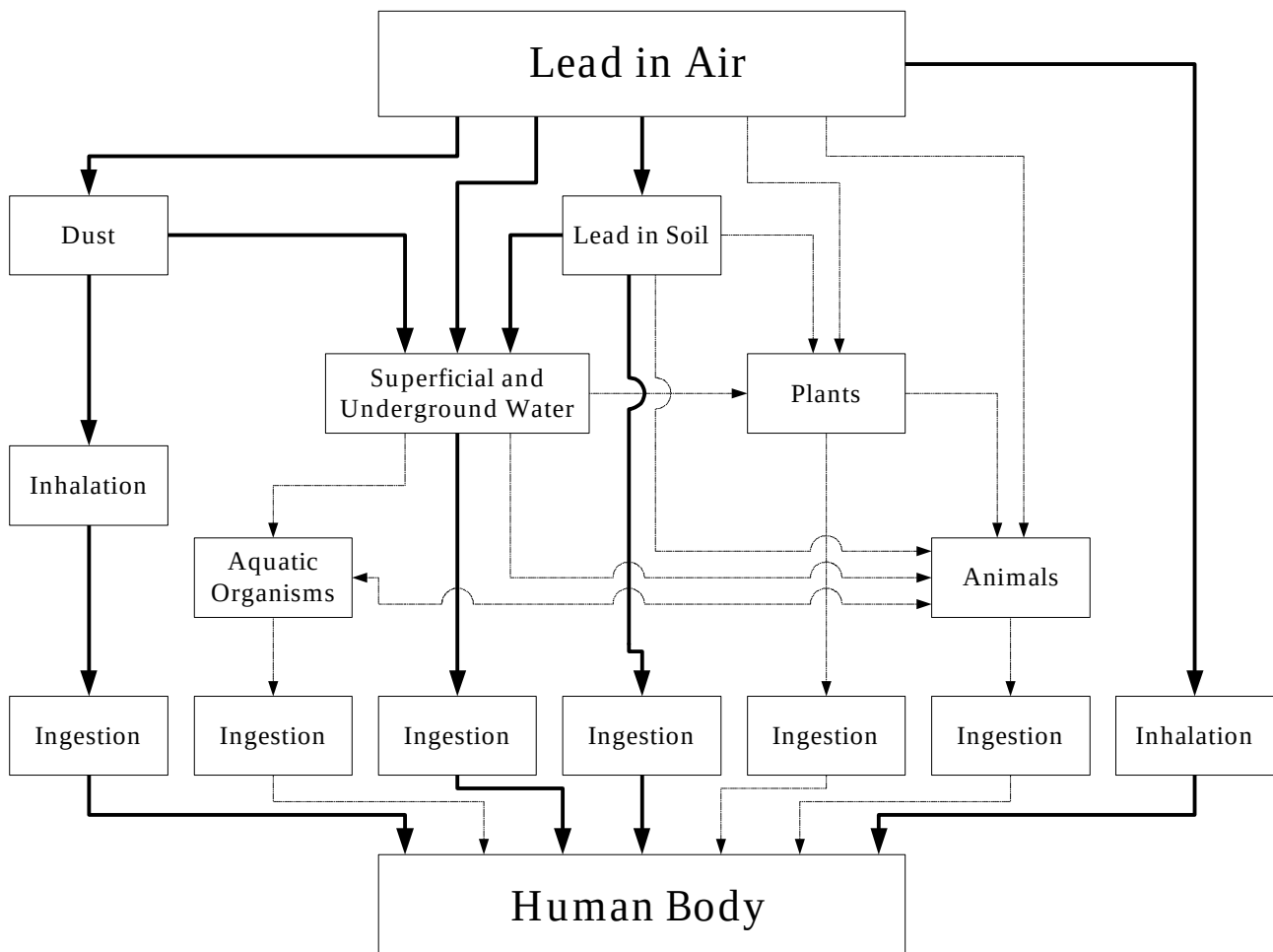


Figure 8: major pathways of human lead intake.

After this observations, the lead-acid battery recycling processes may be considered as a potential and powerful magnifier of the natural lead sources if the proper control actions are not taken, and their influence may be felt in the human health through the bold lines of the figure 8, which represents the most important pathways of human lead intake.

6.2. Toxicokinetics

6.2.1. Absorption, Distribution and Elimination

Lead is absorbed by humans through inhalation, ingestion and skin, although the last one only occurs with rare cases of organic lead contamination and will not be dealt here. The kind of intake route, the size of the particle and the type of lead compound (organic or inorganic), dictate, together, the concentration and possible diffusion of the metal throughout the body. Beside these considerations, the lead absorption depends on other individual characteristics such as physiologic state and tissue integrity, both related to age and other factors such as nutritional, metabolic and anatomic conditions. A general scheme of the lead toxicokinetics may be seen in figure 9.

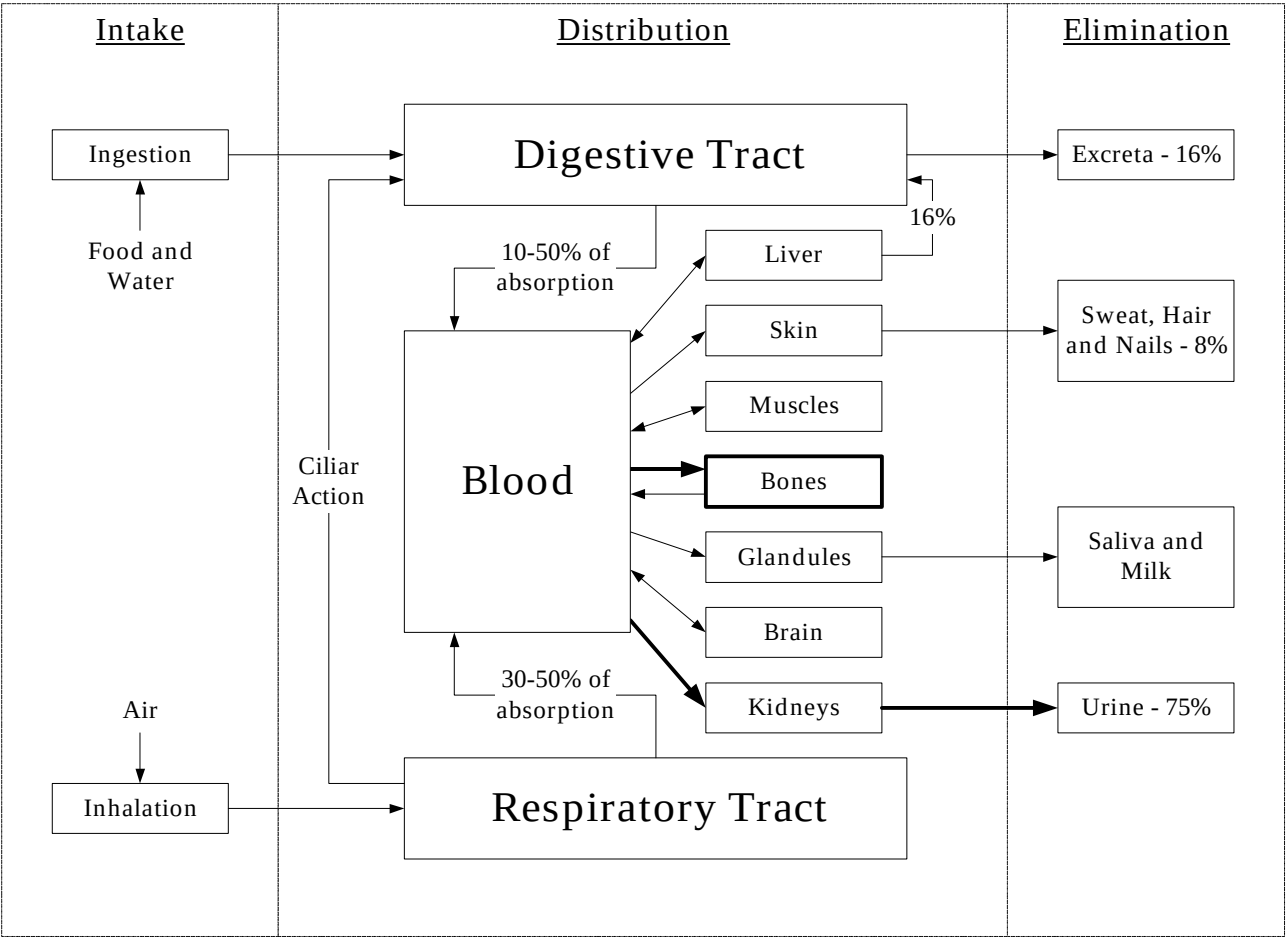


Figure 9: toxicokinetics of lead in the human body

The inhalation route is the main source of lead absorption in the professional environment, being responsible for the occupational hazard observed in lead refining plants if the control protocols are not followed. Despite the fact that the mechanism of absorption is not entirely understood, around

20-40% of the lead that enters the respiratory tract remains in the body, and a major part of it is, by means of ciliar motion, directed from the respiratory tract to the gastrointestinal tract. The amount that remains inside the lungs is rapidly absorbed by a process that is independent of the chemical species of lead involved. It is estimated that a concentration of $1\mu\text{g.m}^{-3}$ of lead in the air produces a concentration of $1\text{-}2\mu\text{g.dl}^{-1}$ in the blood stream.

The gastrointestinal absorption, which is the main non-professional intake route, represents less than 10% of the total lead ingested and is not related to the lead compound involved, actually, the inorganic forms, which are less absorbed in other metal compounds, are the most extensively absorbed in the case of lead compounds.

No matter the intake route, however, children are far more sensitive to lead compounds than adults and some data show that the ingestion may be as high as 50%, i.e. five times greater than adult absorption.

The absorbed lead, both inhaled and ingested, are transported to the blood stream where a rapid equilibrium is established between plasma and red cells in a proportion of 1:16. From the blood stream, the lead is delivered to all organs, specially bones which may retain around 90% of the body lead. Therefore, while the blood lead concentration reflects the recent exposure, bone lead concentration reflects the cumulative exposure.

The elimination of the ingested lead is mainly made by feces, reflecting the poor gastrointestinal absorption rate. On the other hand, the lead absorbed by the body and incorporated into the blood stream is eliminated by urine (75%), gastrointestinal secretions through the liver (16%) and hairs, nails and sweat (8%). Suckling women may also eliminated lead through milk in a concentration very similar to the plasma.

The half-life of lead compounds in the human body is, as a general trend, long, but it varies according to the tissue. Besides, it is almost impossible to determine its elimination rates, since the bones may have a large quantity ready to mobilize into the blood stream. Nevertheless, some half-lives are known for blood (3-4 weeks) and bones (20-27 years).

6.2.2. Toxicity and Health Effects

The toxic mechanism of lead poisoning may be divided in three types: (a) by competing with other essential metabolic metals such Calcium and Zinc; (b) by its strong affinity by sulphidril (-SH) groups in proteins, which means that several proteins may be chemically changed and become more or less unfunctional and reflecting badly in several metabolic paths; (c) and by altering the transport of essential ions throughout the body.

A wide range of heterogeneous of effects and general and unspecific symptoms have been described and associated with lead contamination and they can be found in Annex 2. The most affected human body systems by lead exposure are:

(a) Hematopoietic System: one of the earliest and most important effects of lead contamination in the human body is the alteration in the synthesis of the haem group, leading to anemia as a result of red cell modifications;

(b) Central Nervous System (CNS): the effects of lead in the CNS are much more important to children and neuropsychological effects may occur even for levels considered as sub-toxic, such as $10\mu\text{g.dl}^{-1}$. Prolonged lead exposure may produce important effects over the CNS, causing what is known as saturnine encephalopathy, which symptoms range from subtle psychological and behavioral changes to severe neurological alterations. Besides, there is a difference of effects as the lead source changes from inorganic lead to organic lead.

(c) Peripheral Nervous System (PNS): the inorganic lead produces adverse effects in the PNS, not only in the structure but also in the biochemical behavior of the nerves. The most characteristic effect is the saturnine palsy which the major expression is the lack of strength in the hands.

Beside the above described systems the following systems are also affected by lead contamination: urinary system, gastrointestinal system, cardiovascular system, reproductive system, endocrine system and joints.

6.3. Exposure Limits

6.3.1. Occupational Limits

The establishment of lead threshold limits in air for working places does not ensure that at lower concentrations there will be no adverse effects in those people exposed. Furthermore, it must be considered that:

(a) the present threshold values were determined in developed countries where the labor conditions as well as the health and physical conditions of the workers are very different from those in developing countries;

(b) very often the workers are exposed to various substances that may have synergic or addictive effects with each other;

(c) they were based on adult workers working eight hours a day, five days a week, whereas it is not uncommon to find much longer working journeys and also the employment of children in developing countries.

Besides, it is also important to consider that the general trend of the exposure limits, specially in the case of lead contaminations, is to become lower, i.e. more restrictive, as experimental and clinical techniques become more accurate and capable of detecting important symptoms at lower blood lead concentrations.

Therefore, the threshold limits here presented must be used only as a guide in order to protect those directly exposed, and one must have in mind that the use of a systematic biologic surveillance will be a more accurate indication of what threshold limits should be used for a particular population.

	Concentration/Source
TLV *	0,2mg.m ⁻³ (OSHA, USA, 1981)
STEL **	0,45mg.m ⁻³ for 15 minutes of exposure to smoke and dust of inorganic lead (ACGIH, USA, 1983)
TLV – TWA *** for inorganic lead	0,15mg.m ⁻³ , average value for smoke and dust of inorganic lead (ACGIH, USA, 1984)
TLV – TWA for organic lead	0,10mg.m ⁻³ , average value for organic lead (ACGIH, USA)
TLV - TWA	variable from 30-60µg.m ⁻³ ; 60µg.m ⁻³ to men in fertile age; 40µg.m ⁻³ to women in fertile age (WHO, 1980)

* Threshold Value Level; ** Short Term Exposure Limit; *** Threshold Value Level – Time Weighted Average

Table 1: occupational lead exposure limits

The margins of risk were also established for lead concentrations in blood (Table 2).

	Risk Level			
	Normal	Acceptable	Excessive	Dangerous
Pb concentration in blood (µg.dl ⁻¹)	< 10	40-80	80-120	> 120

Table 2: Lead Exposure Risk Levels According to Lead Concentration in Blood

6.3.2. Environmental Limits

The establishment of environmental limits is in agreement with the concentrations found all over the world in which no adverse effects on the population health was found. On the other hand, differently from the occupational exposure limits that were extensively studied, the environmental limits still need further studies. Therefore, they may be changed in the future as a result of a better understanding of the relationship between lead and the environment and also by the more extensive inventory of lead exposure sources.

The non-occupational lead exposure limits are:

Source	Limit
Potable Water	0,005 mg.l ⁻¹ (WHO, 1984)
Soil	up to 25 mg.kg ⁻¹
Food	3mg/person/week (FAO/WHO 1972 and 1978)
Air	2µg.m ⁻³ - average annual concentration (EC, 1987)
Air	0,7µg.m ⁻³ (URSS, 1978)
Air	2µg.m ⁻³ (EPA, USA)

Table 3: environmental lead exposure limits

6.4. Prevention and Control

6.4.1. *Proposed Actions for Prevention and Control*

From the health point of view, the proposed prevention 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. The most important proposed measures are:

- consider every material containing lead as a possible source of environmental and human contamination;
- keep the work environment in agreement with the national regulations of industrial safety;
- prohibit eating and smoking inside the working areas;
- undertake the development of educational and informative programs;
- demand the use of individual protection equipment in working places containing at least: (a) effectively protective cloth; (b) daily clean-up of the used cloths; (c) protective masks which may vary in accordance of the average lead concentration in air;
- control the lead concentrations in the working environment;
- demand periodical medical control of lead exposed workers.

6.4.2. *Proposed Medical Control*

The most important elements and historical background a doctor should seek for when dealing with lead exposed workers are:

- general health history of the patient;
- occupational history in order to identify other exposures;
- personal history of blood and nutritional diseases;
- neurological history;
- report on the medical examination prior to admission by the employee;
- complete blood count;
- determination of blood lead, ALA-U and ZnPP;
- urine exam;
- electrocardiogram in order to evaluate the cardiac functions;
- take special attention to those workers who smoke and drink or are also exposed to other hazardous or toxic agents.

It must be stressed that the above procedures, not only the proposed actions for prevention and control but also the proposed medical control, should be pursued in order to provide the most clear picture of the contamination situation. It must be remembered that lead exposure and contamination is sometimes misleading and the greater amount of data available the better will be the diagnosis.

With the above described data it is possible, therefore, to establish the temporary incapacity of the worker which shows intoxication signs, provided that a convenient treatment is available.

6.4.3. *Periodicity of Control*

In order to establish the periodicity of the different substance levels in the human body, one should have in mind the local characteristics of at least these aspects:

- general work conditions;
- toxicity of the considered substance;
- concentration of the substance in the environment;

- exposure intensity;
- exposure frequency;
- personal protection degree (i.e. usage of personal protection equipment);
- type of contamination indicator, since there are several of them available and each one is designed to detect and provide a different kind of diagnosis.

As the working conditions worsens, however, a higher control frequency is needed. Experience shows that, apart from the admission exams, yearly based health examinations are the minimum requirement. When worse or critical situations are detected, the frequency may be as intense as one health exam per month.

7. LEAD-ACID BATTERY AND LEAD STATISTICAL DATA

7.1. Primary Lead

7.1.1. Primary Lead: World Concentrate Production

Table 4: world mine production of lead concentrates, 1.998-1.999.

	Mine Production (thousands of tons)	
	1.998	1.999
Australia	618	681
USA	493	520
China	580	501
Peru	260	273
Canada	190	160
Mexico	166	120
Sweden	114	115
Other Countries	659	650
Total	3.080	3.020

7.1.2. Primary Lead: World Metallic Lead Production

Table 5: world primary lead production, 1.998-1.999.

	Primary Lead Production (thousands of tons)	
	1.998	1.999
China	665	730
USA	337	350
Australia	173	240
UK	185	185
Germany	140	174
Canada	130	146
Korea, Republic of	133	140
Japan	144	125
Mexico	163	120
Other Countries	820	800
Total	2.890	3.010

7.1.3. Primary Lead: World Metallic Lead Consumption

Table 6: metallic lead consumption by continents, 1.996-1.999.

	Annual Totals (thousands of tons)			
	1.996	1.997	1.998	1.999
Europe	1.942	1.968	1.952	1.999
Africa	120	121	132	127
America	2.056	2.085	2.177	2.245
Asia	1.795	1.770	1.673	1.810
Oceania	74	70	64	64
Total	5.987	6.014	5.998	6.245

7.1.4. Primary Lead: Uses of Metallic Lead

Battery manufacture is by far the largest single end use for lead, accounting for an estimated 70% for consumption world-wide. Rationalization of world consumption patterns, with reduced dissipative use of lead in the face of environmental concerns, may increase the share of battery sector to over 80% in the near future. Nevertheless, there are wide regional variations on this proportion.

Table 7: uses of metallic lead, 1.999.

Use	Percentage
Lead Batteries	71
Pigments	12
Extrusions	7
Ammunition	6
Cable Sheathing	3

Nevertheless, while there is a wide regional variation on the battery share, in average seventy percent of all lead used yearly in Europe is to produce automobile batteries. In the United States, more than 80% of the lead production is directed toward SLI production.

Table 8: consumption of metallic lead in batteries, 1.993.

Country	Percentage
USA	83
Japan	69
France	65
Germany	56
Italy	46
UK	34

7.2. Secondary Lead

7.2.1. Secondary Lead Production

Table 9: world secondary lead production, 1.999.

	Secondary Lead Production (thousands of tons)	
	1.998	1.999
USA	1.120	1.110
Germany	194	200
Japan	158	168
UK	165	163
France	215	150
Italy	177	140
China	92	129
Canada	136	117
Other Countries	623	633
Total	2.880	2.810

7.2.2. Secondary Lead: Percentage of Secondary Lead in Country Production

There are several countries that depend exclusively on secondary lead production: Austria, Brazil, Colombia, Czech Republic, Ireland, Jamaica, Malaysia, Netherlands, New Zealand, Pakistan, Philippines, Portugal, Slovenia, South Africa, Spain, Switzerland, Thailand, Trinidad e Tobago and Ukraine.

Table 10: percentage of secondary lead production, 1.999.

	Primary Lead	Secondary Lead	Total	% 2° Lead
Argentina	0,4	32	32,4	98,8
Algeria	0,9	6,1	7,0	87,1
Iran	9	38	47	80,8
USA	350	1.110	1.460	76,0
Italy	75	140	215	65,1
Japan	125	168	293	57,3
France	119	150	269	55,7
Germany	174	200	374	53,5
Turkey	4	4	8	50,0
Other Countries	2167	1042	3209	32,5
Total	3.010	2.810	5.820	48,3

7.3. Lead-Acid Batteries

7.3.1. Lead-Acid Batteries: Annual Production

Table 11: estimated production of automobile lead-acid batteries

Country/Region	Production (millions)	Percentage of Total
USA	117	40,3
Europe	87	30,0
Japan	36,2	12,5
Other Countries	49,8	17,2
Total	290	100

7.3.2. Lead-Acid Batteries: Uses

Table 12: uses of lead-acid batteries (% of global market), 1.995

Type	Europe	USA	Japan	Others	Total
Automotive	19.0	30	9.0	13.0	71
Industrial	13.0	8	2.0	1.0	23
Generic	1.2	2	1.5	0.3	5
Total	33.2	40	12.5	14.3	100

The number of automobile batteries produced yearly in a country is directly linked to several factors:

- size and characteristics of the vehicle population;
- vehicle production and number of batteries per vehicle;
- average battery lifetime;
- behavior of internal market and its exporting potential: import and export of vehicles, new batteries, battery scrap, other lead scrap, lead concentrate, refined lead and other lead products.

Table 13: uses of lead-acid batteries in Europe (thousands of tons), 1.995.

Country	Car	Motive	Standby	VRB*	Generic	Total
Germany	128	24	18	7	5	182
France	113	18	15	6	3	155
UK	58	29	13	15	9	124
Italy	90	11	12	4	1	118
Spain	66	8	3	1	-	78
Scandinavia	57	12	7	1	-	77
Others	29	5	2	1	-	37
Total	541	107	70	35	18	771
%	70	14	9	5	2	100

7.3.3. Lead-Acid Batteries :Lifetime

Although there have been no systematic studies on the lifetime of lead-acid batteries in developing countries, it has been suggested that batteries last, in average, 20-24 months in these areas. More precise data is available for developed countries.

Table 14: estimated useful life of automobile batteries, 1.995

Country/Region	Life Time (years)
Western Europe	5,3
Canada	5,0
Japan	4,5
Australia	3,1
United States	3,0
Brazil	2,4
India	1,8

7.3.4. Lead-Acid Batteries: Composition

Lead-acid batteries are constituted by an organic material part, represented by the container, cover and plate separators, and an inorganic part, represented by the lead terminals, connectors, positive and negative plates and the electrolyte. A quantitative description of these parts are depicted below.

Table 15: composition of vehicular and motive batteries

Recyclable Material	Amount (kg)	
	Vehicular Batteries*	Motive Power Batteries**
Lead	8.4	262.7
Plastics	1.1	35.4
Electrolyte	3.8	83.5
Steel	-	58.4
Copper	-	1.7
Total Weight	13.3	441.7

* 12V, 44AH, 220A battery; ** 24V, 500Ah, DIN 43 535 battery

Table 16: average percentage composition of SLI lead-acid batteries

Component	% in weight
Lead Salts and Oxides	50
Acid	24
Metallic Lead	17
Plastics	5
Ebonite and Separators	4
Total	100

Table 17: metal concentration in electrolyte of lead-acid batteries

Metal	Concentration (mg.dl ⁻¹)
Lead, Particulate	60-240
Antimony	20-175
Iron	20-150
Calcium	5-20
Zinc	1-13.5
Lead, Dissolved	1-6
Arsenic	1-6
Tin	1-6

7.4. Recycling Statistics

8. FINAL CONSIDERATIONS

Several important issues related to the recycling of used lead-acid batteries were considered along the previous chapters: history, technical aspects, constitution, recycling process overview, monitoring and control measures, health issues, etc.. However, a complete survey on the lead recycling processes would require a much deeper incursion on industrial processes, economic factors, social aspects and other, which is out of the scope of this technical guideline.

However, some possible targets for further analysis must be indicated:

- ⊗ there are indications that the lead-acid battery recyclability could be further improved by changes in battery design, i.e. plastic case composition, lead plate composition, electrolyte physical state. etc.. However, these changes must be a conjunct effort between producers, recyclers and governments;
- ⊗ other performance indicators, such as Technology Assessments (TA), Life Cycle Analysis (LCA), Risk Assessment (RA), Environmental Auditing (EA) and Environmental Manage System (EMS), should be adopted and used in order to improve the environmental and health protection;
- ⊗ international standards, such as ISO 14000 series, should be pursued;
- ⊗ the formulation and adoption of specific regulations and mechanisms such as ecolabels should be studied as important factors;
- ⊗ it must be realized that planning, regulation design and control methods all depend on data. Therefore, data generation is of utmost importance in order to guide and help decision-makers, and data generation mechanisms, such as chemical analysis, environmental monitoring, historical lead indexes, etc., should be gathered;

Finally, it must be understood that the lead recycling 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. 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.

ANNEX 1 – EIA: SUGGESTED STRUCTURE

1. REGIONAL DESCRIPTION

1.1. General description of the site environment

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1.1.2. *Climatic features*

1.1.3. *Socioeconomic context and soil occupation*

1.2. General description of the site surroundings

1.2.1. *Description of the physical environment*

1.2.2. *Description of the natural environment*

1.2.3. *Identification and quantification of existing wastes and emissions*

1.3. Existing facilities near the site

1.3.1. *Public utilities*

1.3.2. *Urbanism*

1.3.3. *Soil occupation*

1.4. Water Resources

1.4.1. *Regional water use*

1.4.2. *Recycling plant water use*

2. CHARACTERISATION AND CLASSIFICATION OF DIFFERENT IMPACTS CAUSED BY THE PROJECT: CONTROL AND MONITORING MEASURES

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2.3. Environmental impacts at operation phase

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2.3.2. *Gas emissions*

2.3.3. *Soil occupation*

2.3.4. *Noise Pollution*

2.3.5. *Conclusions*

2.4. Water resources and usage

2.4.1. *Use of water*

2.4.2. *Water use limitations*

2.4.3. *Conclusions*

2.5. Liquid Effluents

2.5.1. *Identification and quantification of liquid effluents*

2.5.2. *Summary of the water effluents*

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2.5.4. *Conclusion*

2.6. Gaseous Emissions

2.6.1. *Introduction*

2.6.2. *Continuous emissions*

2.6.3. *Periodical emissions*

2.6.4. *Accidental emissions*

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2.7. Solid, liquid and pasty wastes

2.7.1. *Waste identification and quantification*

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- 2.8. Odors
- 2.9. noise pollution
 - 2.9.1. *Noise source identification*
 - 2.9.2. *Control Measures*
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- 2.10. Movements
 - 2.10.1. *Raw materials*
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3. PROJECT CHOICE REASONS

- 3.1. Technical justifications
- 3.2. Environmental protection justification

4. SYNTHESIS OF ENVIRONMENTAL IMPACTS

- 4.1. Global impacts
 - 4.1.1. *Landscape impacts*
 - 4.1.2. *Roads and traffics impacts*
 - 4.1.3. *Water consumption impacts*
 - 4.1.4. *Water quality impacts*
 - 4.1.5. *Air quality impacts*
 - 4.1.6. *Waste elimination impacts*
 - 4.1.7. *Noise, vibration and light impacts*
 - 4.1.8. *Comparative pictures of before and after project implementation*
- 4.2. Schedule of the control measures in order to decrease environmental impacts
- 4.3. Site recovery after the end of exploitation
- 4.4. Cost Evaluation
- 4.4. EIA Responsibles

5. ANALYSIS OF USED METHODS

- 5.1. List of studies performed
- 5.2. Eventual problems, either scientific or technical

ANNEX 2 - TOXIC EFFECTS OF LEAD IN MAN

It must be taken into consideration that lead is a natural occurring metal, its presence in the human body is inevitable, and the normal range of blood lead levels is 10-40µg.dl⁻¹. Evidence of harmful effects in adults is rarely seen at blood concentrations below 80µg.dl⁻¹ and cases of poisoning usually involve levels considerably higher than this. Besides, symptoms of lead poisoning in children are very different from those in adults and the disease is generally more serious, though signs may appear at lower blood concentrations.

Lead induces a variety of biological effects of which the best recognized refer to the derangement of haem synthesis. These include: inhibition of the porphyrin synthesis enzyme, δ -aminolevulinic acid dehydratase (ALA-D); inhibition of iron incorporation into the porphyrin which results in elevated levels of free erythrocyte protoporphyrins (FEP).

Lead poisoning may occur in two forms: acute poisoning and chronic poisoning:

Acute lead poisoning - in this case, symptoms occur soon after taking a massive amount of lead and rapidly become severe, and it is usually a consequence of accidental ingestion of inorganic lead and may be considered a rare event even for people working in lead recycling plants. Nevertheless, a short description of acute poisoning is provided: a sweet metallic taste in the mouth is quickly followed by symptoms of thirst, or burning abdominal pain and vomiting, followed by diarrhea or occasional constipation; death, if occurs, does so usually within the first two days, and is preceded by collapse with a slow pulse and the patient lapsing into coma; most patients recover however, but attacks of colic and other signs of the poisoning process may persist for a while.

Chronic lead poisoning - it is considered to be the most important kind of occupational exposure to lead sources, in which the body is exposed to lead concentrations usually not so high as in the case of acute poisoning, but high enough to produce observable effects after some time. The chronic poisoning is usually preceded by a sub-clinical and pre-symptomatic stage in which the concentration of lead in the body slowly raises. The earliest symptoms of poisoning in adults are not specific and would not by themselves suggest excessive exposure to lead. Therefore, the diagnosis must be based on a history of exposure, a general feeling of being unwell, and appropriate biochemical tests, since the clinical examination may reveal little of significance: headache, fatigue and lassitude are the most common complaints, and later on loss of appetite, facial pallor and muscular pains occur. If the diagnosis is not made at this stage and treatment started, various body systems start to function abnormally and the results of this gradually become obvious. As the anemia progresses, pallor and shortness of breath increase. Dyspepsia and abdominal colic are most often associated with constipation, but intermittent diarrhea may also occur. At this stage, loss of appetite will have occurred and there may be vomiting; a blue line on the gum margin may be seen and there may also be changes affecting the peripheral nerves and/or central nervous system. Chronic encephalopathy may be difficult to recognize, as in some patients it occurs as depression and other as a manic-depressive state, either of which may be mistaken for an intrinsic mental illness. Occasionally, as the patient may have fits, it is necessary to differentiate poisoning from epilepsy. Damage to sensation rarely occurs, but limb weakness and various changes in nerve conduction have been reported, though gross paralysis is not often seen. Although renal damage is sometimes a part of the condition, impairment of the tubular reabsorption processes and chronic nephropathy are the most common, it is not usually the one which brings the patient for advice since renal failure usually takes place long after lead exposure. In the industrial setting, the earliest clinical effect is nearly always a slight fall in hemoglobin. Most cases progress no further, or may complain of mild non-specific effects mainly affecting the gastrointestinal tract.

Chronic lead poisoning in children - chronic exposure in children takes a somewhat different form. As with adults, the condition may have an insidious onset, the child becoming pale and listless with numerous vague complaints. Brain involvement is likely in serious cases, and is evidenced by drowsiness, clumsiness or difficulty in walking. This may lead on to (or indeed the first sign may be) severe and repeated fits, coma or even respiratory arrest. There is a high fatality rate and of the children that recover, a considerable proportion suffer from permanent damage to the brain. As yet, there is no unequivocal evidence showing whether continued low level but excessive lead intake has any effect on the mental state of the child.

Terminology

Short Term Exposure Limit (STEL): it is an intermediate level between TWA and the Ceiling Level (higher concentration level that must be never surpassed), in which the workers may be exposed for periods of time no longer than 15 minutes by hours, 4 times a day with a minimum period of 60 minutes between each exposure.

Threshold Limit Value (TLV): it is the concentration of the substance in the air of working places under which almost all workers may be permanently exposed without showing any adverse effects.

Time Weighted Average (TWA): is the average exposure concentration of the compound, for an 8 hour work journey, in which the average value, considering all samples, must not be higher than TLV-TWA.

LEGEND

ACGIH: American Conference of
Governmental Industrial Hygienists (USA)
ALA: α -aminolevulinic acid
ALA-D: α -aminolevulinic acid dehydratase
ALA-U: α -aminolevulinic acid in urine
Ag: silver
As: arsenic
Bi: bismuth
Ca: calcium
CaCO₃: calcium carbonate or limestone
Cd: cadmium
Cl₂: chlorine
Cu: copper
CuS: copper sulfide
CNS: Central Nervous System
EC: European Community
EIA: Environmental Impact Assessment
EPA: Environmental Protection Agency
(USA)
FAO: Food and Agriculture Organization
FEP: Free Erythrocyte Protoporphyrins
Fe₂O₃: iron III oxide or ferric oxide
HCl: hydrogen chloride or chloridric acid
Hg: mercury
Mg: magnesium
N₂: nitrogen
NaCl: sodium chloride or common salt
Na₂CO₃: sodium carbonate
NaNO₃: sodium nitrate

NaOH: sodium hydroxide
Na₂SO₄: sodium sulfate
NH₄Cl: ammonium chloride
O₂: oxygen
OSHA: Occupational Safety and Health
Administration (USA)
Pb: lead
Pb²⁺: lead II ion or plumbous ion
PbO: lead oxide
PbO₂: lead dioxide
Pb(OH)₂: lead II hydroxide or plumbous
hydroxide
PbS: lead sulfide
PbSO₄: lead sulfate
pH: water acidity measure
PNS: Peripheral Nervous System
S: sulfur
Sb: antimony
SLI: Starting, Light and Ignition batteries
Sn: tin
SnCl₂: tin II chloride or stannous chloride
SO₂: sulfur dioxide
STEL: Short Term Exposure Limit
TLV: Threshold Limit Value
TWA: Time Weighted Average
WHO: World Health Organization
Zn: zinc
ZnPP: zinc protoporphyrin IX

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