

Technical Guidelines for the Environmentally Sound Management of Waste Lead-acid Batteries



Secretariat of the Basel Convention

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BASEL CONVENTION
ON THE CONTROL OF TRANSBOUNDARY MOVEMENTS OF
HAZARDOUS WASTES AND THEIR DISPOSAL

SECRETARIAT

**Technical Guidelines for the Environmentally
Sound Management of Waste Lead-acid Batteries**

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INTRODUCTION

1. 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, the recycling process may be a potentially dangerous process if not properly controlled. These technical guidelines are, therefore, meant to provide guidance to countries which are planning to improve their capacity in order to manage the used 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:

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

2. One should note, however, that no technologies will be covered in these guidelines. 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?

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

- (a) **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;
- (b) **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 waste production, especially the primary extraction waste;

(c) **energy conservation** – since few metals occur in nature as readily usable forms, the recycling processes allow the production of metals with about 25% or less¹ of the energy used in the primary processes. Furthermore, since most of the primary metal processes require energy-intensive procedures which usually depend on fossil fuels, as in furnaces for example, the recycling processes provide a means of pollution reduction.

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

(a) **toxicity toward the environment and human health** – it is well known that the consequences of lead exposure, being it human or environmental exposure. Thus, it is reasonable to think that lack of a lead recycling system would increase dramatically the risk of exposure since the lead waste would have to have environmentally unsound destinations;

(b) **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;

(c) **large market** – lead enjoys a large market and, depending on the country, a reasonably well-organized collection system of up to 96% from one predominant product which has a short and predictable lifetime: the starting, lighting and ignition (SLI) battery.

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

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

¹ Heinstock, ICME study

1. HISTORICAL BACKGROUND

7. 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, 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 for producing metallic lead by reductive melting in the presence of carbon sources slowly spread from China to the Middle East and from there to Africa along the VI and V millennia BC. In pharaonic Egypt, lead compounds were 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.

8. 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.

9. Marcus Vitruvius Pollio, a first 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 colour of the workers in lead factories of that day, noting that the fumes from molten lead destroy the "vigour of the blood". On the other hand, there were many who believed lead to have favourable 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 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.

10. 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 it also found a new use with the discovery of printing.

11. 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 (the SLI battery).

12. 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.

13. 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 19th century. It was estimated that the lead consumption since the prehistoric period would hardly have passed thirty million tons until that time and the actual consumption was around five million tons a year.

2. TECHNICAL DATA ON LEAD-ACID BATTERIES

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 lifetime.

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 releasing this energy when connected to an external consuming circuit. A **Lead-Acid Accumulator or Lead-Acid Battery** is an electrical accumulator in which the active material of the positive plates is made up of lead compounds and that of the negative plates is essentially lead, the electrolyte being a dilute 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.

(a) **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;

(b) **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 polyethylene and the once popular PVC, paper card or other porous materials 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

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

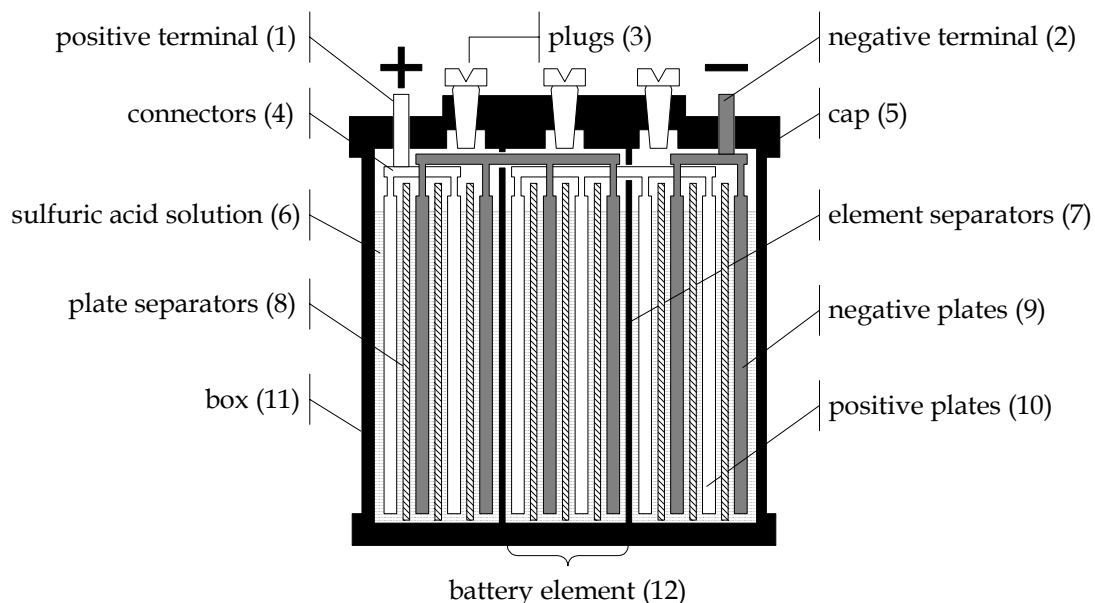


Figure 1: Lead-acid battery components and internal structure

(a) **positive (1) and negative (2) terminals:** made of lead, and where the external electricity consumer devices are connected;

(b) **plugs (3):** one for each battery element, where distilled/deionized water can be replaced whenever needed and also to provide an escape route for gases formed in the cells;

(c) **connectors (4)**: made of lead, that make electrical contact between plates of same polarity and also make electrical contact between separated elements;

(d) **cap (5) and box (11)**: originally made of ebonite, but now more commonly made from either polypropylene or co-polymer;

(e) **sulfuric acid solution (6)**: the electrolyte of the battery;

(f) **element separators (7)**: usually a part of the box and made of the same material, provide chemical and electrical isolation between the electrical elements. They are connected in a serial layout in order to increase the final voltage of the battery;

(g) **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;

(h) **negative plates (9)**: constituted by a metallic lead grid covered by a lead dioxide (PbO_2) paste;

(i) **positive plates (10)**: constituted by metallic lead plates;

(j) **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.

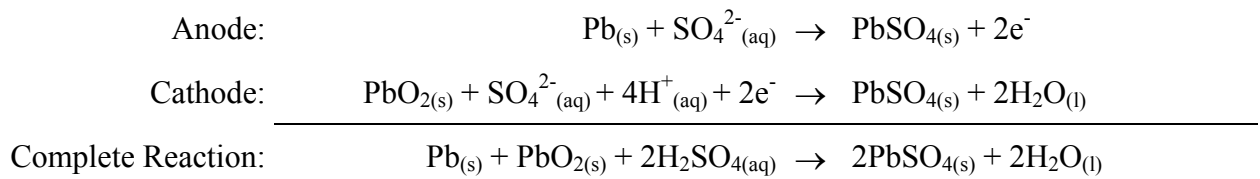
15. The battery plates are constituted by metallic lead structures, known as grids, covered by a lead dioxide paste, in the case of the negative plates, or by a porous metallic lead paste, in the case of the positive plates. The lead used in both the plates may also contain several other chemical elements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

16. After being shaped, the battery plates are placed so 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 has 6 elements in series producing (2V x 6 elements) 12 V.

17. 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

18. When the battery provides electric energy to an external device, several chemical reactions take place at the same time. At the positive plates (cathode) a reductive reaction takes place when the lead dioxide (PbO₂) is converted into lead sulfate (PbSO₄). 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 (H₂SO₄), 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:



19. 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.

20. 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.

21. The discharge-recharge process can be repeated several hundred times with a good response of the battery, but the lead oxide plates become increasingly contaminated by lead sulfate which eventually inhibits the chemical reactions at the lead oxide plates. In addition 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, at this moment the battery is “spent” and becomes a “used lead acid battery (ULAB)”.

2.4. Types and Applications

22. 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:

(a) **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.;

(b) **generic** - batteries used in portable tools and devices, domestic alarm systems, emergency lights, etc.;

(c) **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;

(d) **motive** - batteries used to transport loads or people: fork lift trucks, golf carts, luggage transportation in airports, wheelchairs, electric cars, buses, etc.;

(e) **special** - batteries used in specific scientific, medical or military applications, and those that are integrated in electric-electronic circuits.

2.5. Lifetime

23. The battery life is defined as the period of time in which a battery is capable of being recharged and retain the charge applied. Once the battery is no longer capable 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 can no longer migrate from or to the plates or electrolyte due to lead sulfate coating, and the reactions which produce the electric energy cease.

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

(a) incomplete charging process;

(b) battery remains too long without use or stands a long time between two charges;

(c) hot weather: it increases the sulfatation process rate;

(d) deep discharging process, the deeper the discharge the less life time the battery will have;

(e) low electrolyte level: air exposed plates becomes sulfated immediately.

25. When all this factors are considered together, the battery life span ranges from 6 to 48 months, yet only 30% of all batteries actually reach the 48-month mark. However, some procedures may be adopted in order to extend the battery life:

(a) battery labeling should address the correct procedures to prolong battery life, such as adding just distilled water or usage tips, thus providing information for consumers in order to avoid the above mentioned problems;

(b) addition of additives in order to reduce the build up of sulfates on the active surface of the plates, despite the fact that the use of additives may pose problems to the sulfuric acid recycling;

(c) adoption of new and improved recharging processes that may increase the battery lifetime.

26. At the end of its life the battery is classified as a hazardous waste under the Basel Convention and should be handled accordingly in order to prevent damage to human health or to the environment.

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

3.1. Pre-Recycling Steps

27. Before reaching the recycling plant, used batteries must be collected, transported and stored with proper care, in order to avoid adverse health effects 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

28. 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 network which provides a continuous flow of leaded scrap materials to the recycling process.

29. Experience has shown that, as a general trend, the most spontaneous process of used lead-acid batteries collection 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 with the lead content in the used lead-acid batteries.

30. Although this collection process should be used in favour of an 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:

(a) **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 requires workers to be protected in order to minimize any risk of injury, 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 risk of an accident dramatically, the drainage at collection points it should be avoided;

(b) **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 be sealed and used as the transport container as well minimizing the risk of an accidental spillage. However, this is not often the case and the following short set of storage guidelines should be adopted:

- (i) 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;
- (ii) the storage place must be sheltered from rain and other water sources, be equipped with a water collection system, and also, if possible, away from heat sources;

- (iii) the storage place must have a ground cover, preferably acid resistant concrete 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;
- (iv) the storage place must have an exhaust ventilation system, or simply a fast air recirculation system, in order to avoid hazardous gas accumulation;
- (v) the storage place must have a restricted access and be identified as a hazardous material storing place;
- (vi) any other lead materials which may eventually arise, such as plumbing, should be conveniently packaged 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.

(c) **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 specific demands. Nevertheless, storing large amounts of used batteries, or for a long time, increases the risk of accidental spillage or leakage and this must be avoided;

(d) **collectors must not sell their batteries to unlicensed lead smelters:** since unlicensed smelters are one of the main sources of lead contamination, both human and environmental, it should be stressed that collection points must not sell or send their used batteries to establishments that do not follow high protection standards.

3.3. Transporting

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

(a) **used batteries must be transported inside containers:** no matter which mode of transport is being used, i.e. boat, train, etc., used lead-acid batteries must be transported inside sealed containers due to the risk of leakage, which may be high even if the batteries are appropriately transported in upright position. The transport may displace the batteries from their original positions, including eventual box breakages or turning them upside down, which will certainly leak the electrolyte content, thus making it necessary to provide a shock resistant and acid resistant sealed container;

(b) **containers must be well packed to the transport vehicle:** containers should not be allowed to move while being transported. Therefore, they must be bound, shrink wrapped or stacked properly to avoid this problem;

(c) **the transport vehicle should be identified with symbols:** the vehicle, whether it is a ship a truck or a van must be correctly identified, following international conventions, symbols and colours, identifying the fact that corrosive and hazardous products are being transported;

(d) **specific equipment:** a minimum set of equipment necessary to combat any simple spillage or leakage problems should be provided and the transport team trained on how to use it;

(e) **drivers and auxiliaries should be trained:** people dealing with hazardous wastes should always be trained in emergency procedures, including fire, spilling, etc. and how to contact emergency response teams. Besides this, they should be aware of the specific kind of hazardous material is being transported and how to deal with it;

(f) **personal protection equipment:** PPE should be provided for the transport team and they should be trained in the use of the equipment, in case of any accident;

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

32. The above mentioned points are not an extensive list. Much more specific training 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 badly affected by the effects of spillage in the event of an accident.

3.4. Storing

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

(a) **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 is directed to effluent treatment plant and the batteries are stored empty and ready to be recycled;

(b) **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;

(c) **batteries must be stored in a proper building 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 covered bay, or in the worst case an uncovered place, should be constructed to store them and must have a minimum set of characteristics:

- (i) it must have an impermeable and acid-resistant floor;
- (ii) it must have an efficient water collection system which directs spilled solutions toward the effluent or acid electrolyte treatment plant;
- (iii) it should have only one entrance in and one exit, which should stay closed unless otherwise necessary, in order to avoid dust release;
- (iv) 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 in order to avoid the concentration of toxic gases;
- (v) it must be provided with appropriate fire fighting equipment². Although it is unlikely that a fire happens due to the batteries themselves, it must be remembered that accidents by other causes could set fire on the batteries due to their high content of carbon compounds, such as the plastic boxes. Therefore, fire fighting equipment is necessary;
- (vi) only authorized personnel should be allowed to enter the storage area.

34. 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. In particular, and wherever possible, the storage area should be an acid resistant pit below ground level so that the acid does not leak out of the storage area. Such a storage area requires a sump collection and pump system to remove excess liquids from the bay and safety barriers to prevent trucks falling into the pit when they discharge their loads. Efficient ventilation is also a key element of such a design.

² NOT WATER, in order to prevent the production of the toxic gases such as arsine and stibine.

4. LEAD-ACID BATTERY RECYCLING

35. The pre-recycling steps are finished 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 breaking or breakage;
- (b) lead reduction;
- (c) lead refining.

4.1. Battery Breaking

36. No matter which recycling technology is to be adopted, the batteries must always be drained before they enter 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.

37. Classic methodologies of lead recycling processes, including Water-Jacket Blast furnaces, reverberatory furnaces, electric arc furnaces, and short and long rotary furnaces, do not require battery breakage before the smelting process. The drained batteries are entered directly into the recycling process since pyrometallurgical techniques accept organic materials and other substances, which are burned or incorporated into the slag.

38. However, processes in which the batteries are broken prior to the recycling process are preferable due to:

- (a) increase in the percentage lead production and decrease in the slag formation;
- (b) possibility of soft lead³ 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.

39. 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 the recycling process.

³ Low Antimonial or Antimony free lead

4.1.1. Historical Background of Battery Breaking

40. Before the 1960's, 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, especially in the developed ones, unfortunately it has not in most developing countries. It must be stressed, however, that manual breaking 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 environmentally unsound management of these wastes. Nevertheless, some modern smelting plants still require manual breaking of big industrial batteries that cannot be broken by 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.

41. During the decades of 60's and 70's, the battery breaking evolved into a mechanical guillotine or saw that greatly reduced human contact with the breakage process. They were also supplemented by automatic feed and were the first examples of entirely mechanized systems, some of them are still in use.

42. From the 1980 onwards, 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 Breaking Process

43. The modern battery breaking 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 breaking apparatus by means of automatic mats or small wagons whenever possible.

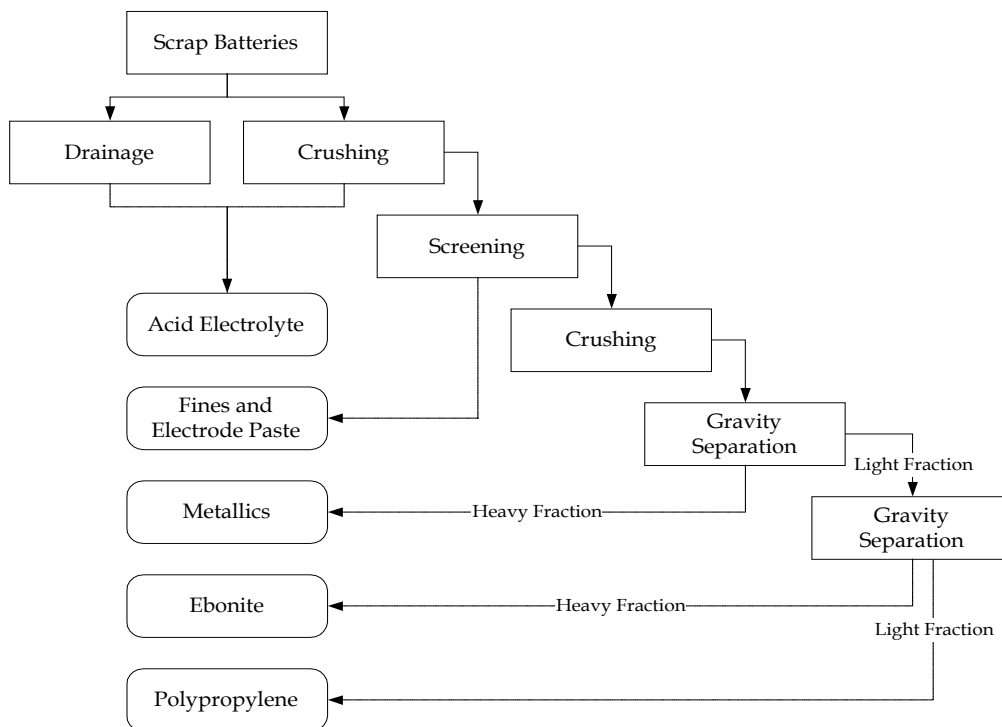


Figure 2: Battery breaking process.

44. Once the batteries arrive at the breaking machine, they are processed in the hammer mills, or other crushing mechanisms, that break them into 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.

45. After breakage, the lead oxides and sulfates are separated from the other materials by gravity in water by a system of moving mesh conveyers. After separation, they are directed to a furnace, in case of pyrometallurgic techniques, or for other processes, for example hydrometallurgical techniques.

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

47. 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 granular pieces of lead oxide and sulfates and the third one is the heavy layer consisting 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.

48. 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 washed to remove traces of lead oxides, 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.

49. Battery breaking 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. Nevertheless, every effort should be made to eliminate the use of manual battery breaking and the health and safety risks that are associated with this practice. If mechanical battery breaking equipment is unavailable, for whatever reason, the safest approach to prepare the battery for smelting would be the following: puncture and drain the electrolyte for the battery and treat it accordingly; remove the top of the battery complete with plates and separators using a circular saw and observing the correct use of guards and protective equipment; send the plates and grids with the top of the battery to the smelter; return the battery case to the manufacturer for reuse.

4.1.3. Battery Breaking: Potential Sources of Environmental Contamination

50. This section, and the other two sections in the lead reduction and lead refining processes, is not designed to describe or extensively list all possible sources of contamination that may occur in the lead recovery processes, since this is almost an impossible task. It is designed, instead, to itemize just a short and predictable list of common contamination sources and where to look when searching for them. Specific sources of contamination will have to be determined in the light of the process employed. Methods of contamination prevention will be treated in the environmental protection chapter. That stated, the common sources of environmental impacts in the battery breaking process are then:

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

(b) manual battery breaking – *source of human health injury and environmental damage through heavy spillage and lead contaminated dust formation*: manual breaking usually relies on primitive tools, poorly protected workers and no environmental protection whatsoever. The situation is even worst in the case of sealed batteries, which are not easily drained, increasing dramatically the risk of heavy spillage and damage to human health. Therefore, it should be avoided at all costs;

(c) mechanical battery breaking – *source of lead particulate*: the process of breaking batteries through crushing on hammer mills may spread lead particulate. However, the fact that the mill is sealed and uses copious quantities of water the formation of such particulates is prevented;

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

(e) plastic and ebonite chips – *contaminated wastes*: ebonite scraps removed from the breaking process may pose a problem, since they are usually contaminated by levels as high as 5% (w/w) of lead. Therefore, it is important that the final traces of lead are removed by a second wash, preferably in an alkaline solution, followed by another rinse prior to further treatment or disposal.

4.2. Lead Reduction

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

4.2.1. Pyrometallurgical Methods

52. 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 fluxing and reducing substances (figure 3).

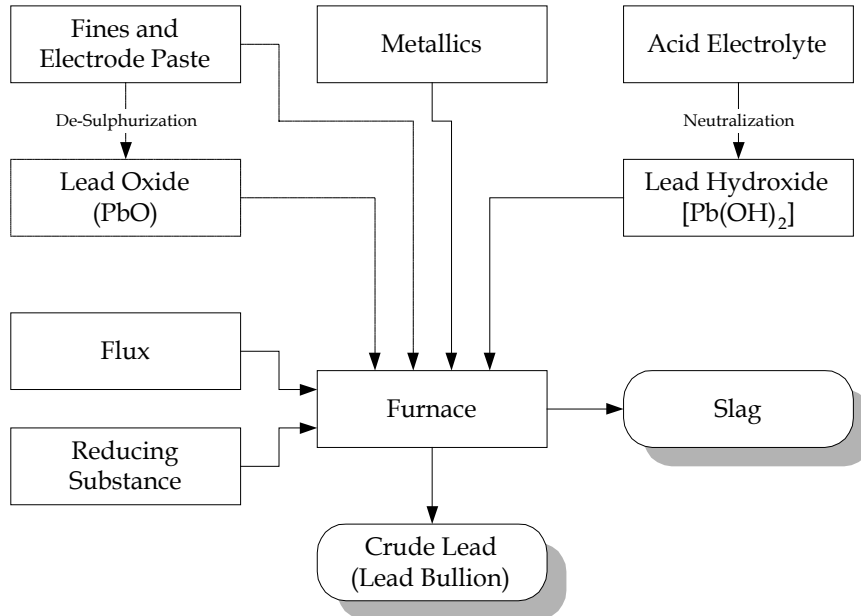


Figure 3: Diagram of a lead smelting process

53. Prior to smelting, some methods may be employed to 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) to 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 into the air. However, other methods simply add controlled amounts of lead sulfate as well as de-sulphurizing agent directly into the furnace.

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

55. 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 these guidelines.

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

57. Reducing agents, on the other hand, are added with the purpose of reducing the lead oxide (PbO) and hydroxide [Pb(OH)₂] to metallic lead. It is usually a carbon based compound such as coke, coal fines or other natural carbon source.

58. The quantity of flux and reducing agent 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.

59. After the process had been properly balanced, the melted metallic lead starts to accumulate in the bottom of the vessel. However, as mentioned earlier, it is sometimes heavily contaminated with other metals of economic value. Therefore, this lead bullion must undergo a refining process before pure lead can be recovered from it.

4.2.2. Hydrometallurgical Methods

60. 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).

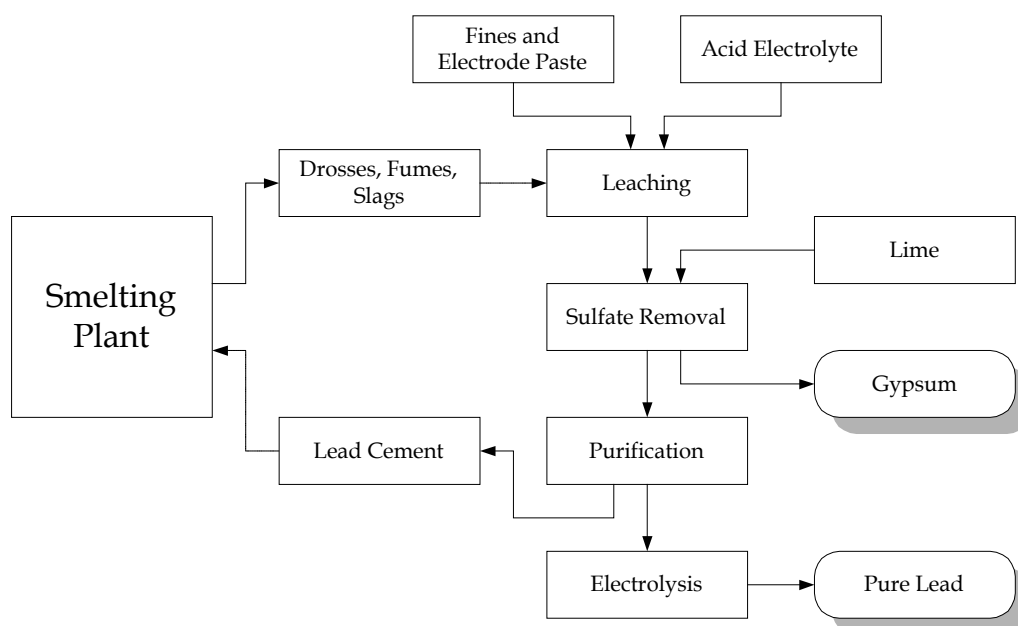


Figure 4: Diagram of an electrolytic lead process

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

62. 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).

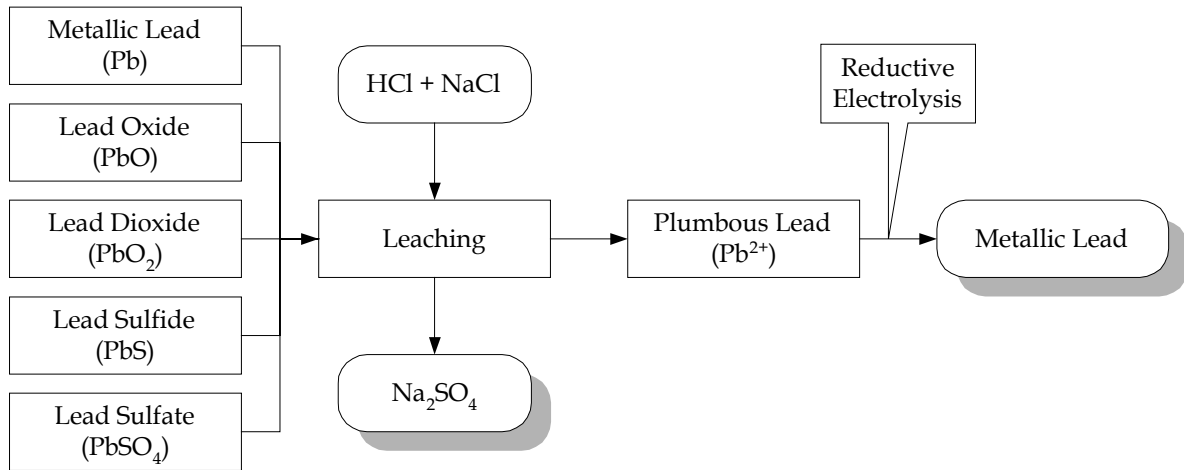


Figure 5: Electrochemical process in hydrometallurgical lead production

63. The electrolysis deposits lead as dendrites or sponge, which are subsequently shaken off and collected on a conveyor belt and pressed to form platelets of pure lead (99.99%), which can then be conveyed to a melting kettle for casting into ingots. The whole extraction process can be run continuously 24 h/d, without interruption.

4.2.3. Lead Reduction: Potential Sources of Environmental Contamination

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

(a) lead compounds derived from the breaking process – *lead and lead compounds in dust and water*: the separated and fine materials from the breaking process are usually wet, since the main processes of separation are based on water techniques. However, if they are not incorporated in a fully automated process, they will have to be transported from the breaking facility to the reduction facility and some muddy and/or watery material may spill and fall from the transport system. After drying, these materials become a powder and may contaminate the factory and its surroundings as fine lead dusts;

(b) drosses – lead contaminated materials: drosses are formed while the fusion process takes place. Its function is to remove materials that are not easily incorporated or wanted in the crude lead. However, these drosses still contain lead that can be recovered and are recycled in the fusion process. In order to accomplish these task, the drosses must be removed and transported to the furnace charging bay, but since they are usually a dusty material and occasionally powdery (copper dross), they may be a source of lead contamination while being transported;

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

(d) 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 furnace conditions, 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 mixture of iron and sodium based compounds producing sodium skims and pyrites. Ebonite also has 6-10% of sulfur that may contribute to the SO₂ emission if it is added to the furnace charge;

(e) organic material combustion – tar formation: a well structured and controlled refinery does not need to worry about tar formation, since its reduction process consumes all organic materials. On the other hand, the less controlled the reduction process is, the greater are the tar emissions, especially in artisan foundries. If the reduction furnace has filters, the emission of tars is an even greater problem since they are very pyrogenic and may produce fires in the filtration plant, thus increasing the risk of an accident and the possibility of a rogue emission. The introduction of afterburners to complete the combustion of gases from the furnace is the usual solution to this problem, but a complete restructuring of the process, removal of organics for example, may present better perspectives;

(f) chlorine (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 furnace increases the chances of chlorine emissions. The major part of it is absorbed by the basic skims of calcium or sodium, however some of the chlorine is chemically converted into lead chloride which is volatile under furnace conditions but captured by dust filters as the temperature decreases;

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

4.3. Lead Refining

65. As indicated earlier, 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 bullion 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 the soft lead standard does not allow more than 10g per ton of these metals.

66. 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

67. Thermal refining is performed in liquid phase, which means that the crude lead must be melted to temperatures higher than 327°C (lead melting point), but less than 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.

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

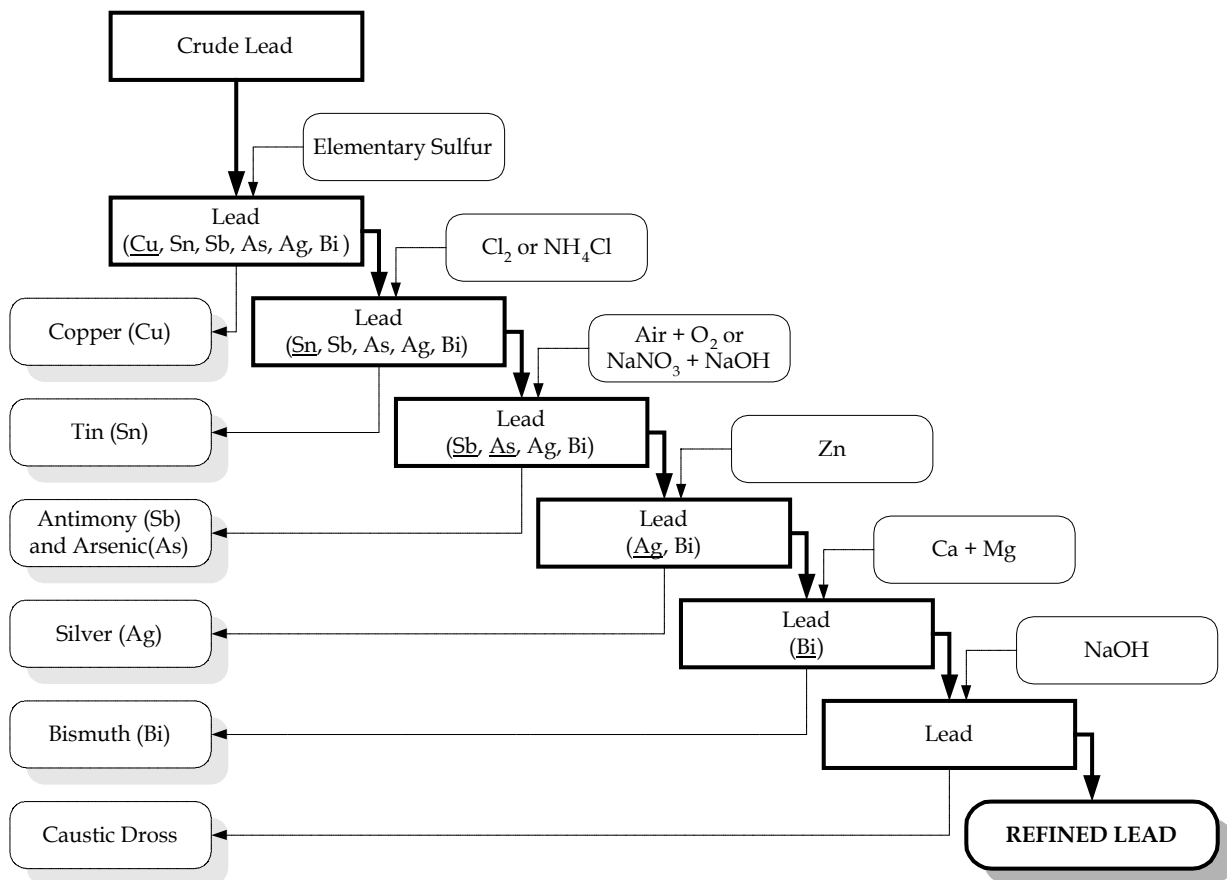


Figure 6: Pyrometallurgical lead refining

69. Copper (Cu) is the first element to be removed with elemental sulfur in a two phase procedure. In the first step, almost all copper is removed as a copper sulfide (CuS) skims when elemental 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 elemental sulfur to the molten lead at 330°C until no further reaction takes place. As the use of sulfur requires strict health and safety requirements to prevent fires and choking from acrid fumes a safer alternative is to use iron pyrites thereby eliminating the risk of fire and acrid fumes.

70. The tin is usually removed in the smelting process and only needs removal in the refining stage if scrap lead grids and other solid lead materials have been added to the refining kettle and allowed to melt into the molten bath. The tin is so unstable that just stirring the bath and adding some sodium nitrate (NaNO₃) is usually sufficient to remove it. If there is still some residual tin it can be removed using an air lance in the kettle.

71. 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. Then the resulting skims are a mixture of oxides (25% Sb, 10% As and 65% Pb).

72. 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).

73. 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.

74. The pure lead is then treated with sodium hydroxide (NaOH) to remove any residual 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 bullion, which is reintroduced in the smelting circuit.

4.3.2. Lead Refining: Potential Sources of Environmental Contamination

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

(a) over heated lead – *lead fumes*: sometimes the lead from the reduction process is introduced directly into the refining kettle, which may be as hot as 1,000°C. Therefore, it is not uncommon that the lead refining process produces large amounts of lead vapor. Ideally lead should be tapped from the furnace directly into a lead bath or allowed to cool prior to pouring;

(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. The use of iron pyrites eliminates this problem;

(c) skim production and removal – metal contaminations: the skim production and removal from the refining kettle while refining unwanted metals from the crude lead may pose threats to the human health and environment due to the physical characteristics of the skims. Sometimes they are in the form of a very fine and dry dust with a high percentage of lead and other metals, it is important to provide adequate covered or sealed transport, storage and a sound destination to this potentially hazardous by-product;

(d) chlorine (Cl₂) tin (Sn) removal and recovery – chlorine gas release: If the tin is removed by chlorine gas for later recovery, then this is a very delicate procedure. The intake of gas is planned in order avoid chlorine release, i.e. the gas reacts with the tin before reaching the surface of molten lead. However, an uncontrolled addition of chlorine may release the poisonous gas to the environment. Besides, the storage and handling of chlorine is itself a delicate operation due to its corrosiveness and toxicity;

(e) oxygen (O₂) enriched air tin (Sn) removal – lead fume: 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 fume.

5. ENVIRONMENTAL CONTROL

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

77. The environmental control process may be divided into three main subjects according to the sophistication of the recycling plant: (a) the recycling plant may have not yet been commissioned; (b) the recycling plant was constructed some time ago 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)

78. 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 financing are released after the study has been presented to and approved by the governmental agencies.

79. 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 opportunity to make changes in the project at minimum costs and also to plan ahead in terms of best available and most appropriate 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, and so on.

80. 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, especially alternative sites;

(h) dimensions, technologies employed, raw material sources, energy sources and products;

(i) justification for the employed methods and technologies;

(j) finally, the EIA must be a concise and objective report, and value judgments must be avoided as much as possible.

81. 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

82. If an EIA was not performed before the implementation of a lead recycling plant, it is likely that the facility has some technological and environmental problems to resolve, 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 instigation 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*

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

5.2.1.1. Acid Electrolyte and Effluents

84. The direct discharge of these liquids into the environment without treatment would comprise a huge environmental impact. A suggested approach to this problem would be to try to stabilize 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 battery 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 to the cement industry or the building trade;

(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.

85. Every lead recycling plant should have an effluent treatment station in order to treat the water that 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

86. All stages in the battery recycling plant can release some sort of smoke or dust, which must be collected and either returned to the plant or 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.

87. The so-called “mechanical” dust, i.e. particulate material with large physical characteristics, is relatively easy to filter and remove from air. However, the finer the dust, the more difficult it is 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 redirected toward the smelting plant in order to recover the lead.

5.2.1.3. Fugitive Emissions

88. Fugitive emissions are atmospheric discharges from raw materials and/or industrial processes that are released to the atmosphere without passing through any filtering device or control mechanism designed to reduce or eliminate the hazardous content or amount of the materials being produced prior to release to the environment.

89. Several potential sources of fugitive emissions can be identified from topics already covered in the section dealing with the control measures taken for storage facilities, battery breaking processes, lead refining, and so on, but also from the "red" hot molten lead as it is drained from a smelting furnace caused by the high vapor pressure of lead and its compounds at about 1000°C. In the same context, fugitive emissions would be generated if lead furnace bullion is transferred in an open ladle or “pot” at about 1000°C and poured into a refining kettle, and later during processing if the dusty dross is skimmed manually without extraction or ventilation.

90. Basically, there are two ways of controlling fugitive emissions:

(a) by controlled ventilated tapping of the furnace bullion into a casting mould to allow the bullion to solidify. Only when the lead block has solidified will it be moved to the refining kettle and then gently melted into a liquid bath of molten lead. Any dross produced would be removed in a procedure that ventilates the working area and extracts and contains any dust produced in a baghouse filter system.

(b) by tapping the red-hot molten lead from the furnace into a bath of molten lead, where the lead bath is about twenty degrees above the freezing point of lead and well below the temperature that can produce fugitive emissions. The bath of molten lead must be covered and ventilated so that any emissions would be removed to the baghouse. As the refining kettle containing the bath of molten lead fills, the lead may be pumped to another kettle in order to start the refining process.

5.2.1.4. Sulfur Dioxide (SO₂) Elimination

91. 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 furnace as a slag formation reagent. Even after filtration and removal of dust, however, the gases will still have small quantities of vestigial dust and SO₂.

5.2.1.5. Use of Oxygen (O₂)

92. Oxygen (O₂) is used to enrich the gases that are 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 furnace;

(c) increase in the furnace production.

93. Therefore, the use of pure oxygen (O₂) to enrich the air supply to the furnace burners provides a much cleaner production process.

5.2.1.6. Flux Agent Choices and Slag Stabilization

94. Calcium slag, formed by the addition of calcium carbonate (CaCO₃) flux to the furnace, produces a non-leachable slag, which means a more environmentally sound waste. On the other hand, it increases the working temperature of the furnace and releases more sulfur dioxide (SO₂), which means more energy costs and alterations in the furnace performance, particularly the life of the refractories. Furthermore, 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.

95. Stabilizing the slag, which ultimately means controlling the fusion-reduction-refining steps very well, would be a huge step toward cleaner production, since this is the major hazardous waste formation in the whole process. The sodium slag, 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.

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

5.2.1.7. Heavy Organics Recycling

97. The heavy organic fraction is constituted by plate separators and 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 slag, tar formation and others, did not lead to a conclusive report and further studies are required, but this is a promising destination for these wastes.

5.2.1.8. Polypropylene Recycling

98. Polypropylene is such a valuable product that it alone could sustain the lead-acid battery breaking. Therefore, reprocessing of the plastic components should be seen as a profitable activity that, unfortunately, is not universal.

5.2.1.9. Sound Destination to Unrecoverable Wastes

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

5.3. Environmental Monitoring

100. 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.

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

5.3.1. *Control Measures*

102. Independent of the pollution control technologies employed at 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. However short, the list provides some useful ideas in achieving good environmental control practices.

(a) **personal protection equipment (PPE)**: all workers must have their own PPE, 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 properly according to the manufacturers specification and all sections of the recycling plant should have clear and visible

identification of what PPE a worker should be using while in that specific sector. The minimum PPE requirements would be respirators, hard hats and safety footwear;

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

- (i) prohibit smoking in the working place;
- (ii) segregate the work and eating areas;
- (iii) enforce showering at the end of work;
- (iv) change out of work clothes before going home;
- (v) change and launder workwear daily;
- (vi) check and clean respirators daily.

(c) **breaking, reduction and refining operations inside enclosed buildings:** allowing the collection of all dusts through a convenient filtering system and avoid the release of contaminated dusts to the atmosphere;

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

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

(f) **slag storage:** hazardous materials should be stored with the same degree of care as 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 for battery storage (paved soil, covering, etc.) apply to slags, drosses, skims and other hazardous by-products, wastes and materials;

(g) **air filtering system:** it should be as close as possible to the ventilation area and all extraction systems should be a closed system to avoid dust release;

(h) **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;

(i) **trucks and transports should be washed when leaving the recycling plant:** especially wheels and the 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;

(j) **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 suitably trained personnel;

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

103. Independent of the pollution control 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*

104. Environmental monitoring may be thought of 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 regarded as a huge source of environmental contamination. Therefore, it should be done by every lead recycling plant.

105. Some monitoring targets are:

(a) **effluents:** after being treated at the effluent treatment station, all the 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);

(b) **gases:** there must be 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;

(c) **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;

(d) **air quality:** there must have a continuous monitoring of the air quality inside the enclosed buildings such as in the battery breaking facility, etc.;

(e) **medical surveillance:** all workers must be monitored for their health and a record must be kept. The immediate surrounding population should also be offered a free check-up periodically.

106. Although these monitoring activities are costly and several of them need specialized personnel, which may 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

107. 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 framework (figure 7).

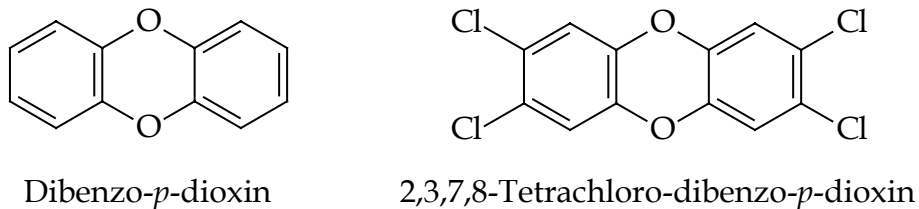


Figure 7: Dioxin molecular framework and 2,3,7,8-TDD

108. 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.

109. 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.

110. 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:

(a) 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;

(b) activated carbon can be injected into the gas stream in order to absorb the organic molecules and, afterwards, be filtered. The filtered dust must be treated as a hazardous waste and must not be directed to the furnaces, but instead incinerated in specialized facilities or treated with extreme care;

(c) catalytic oxidation has been reported as an efficient method for dioxin destruction.

111. These and other available techniques, especially maintaining complete combustion of all furnace materials at high temperature, must all be considered according to the specific constraints 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

112. 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.

113. 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.

114. Since the human body does not discriminate 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.

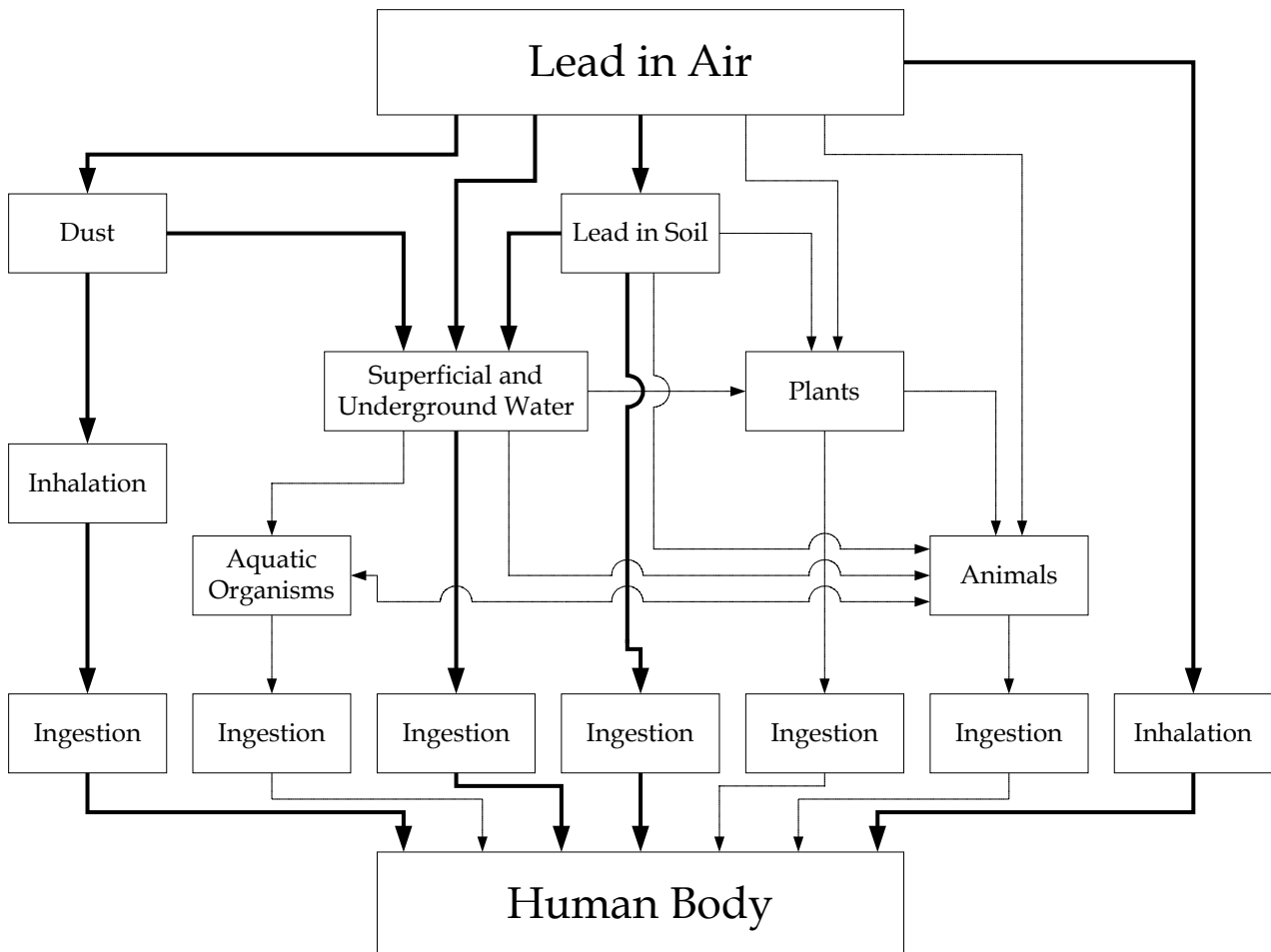


Figure 8: Major pathways of human lead intake

115. After considering these observations, the lead-acid battery recycling processes may be considered as a potential and powerful magnifier of the natural lead sources if the proper controls 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*

116. Lead is absorbed by humans through inhalation, ingestion and skin, although the last one only occurs with rare cases of organic lead contamination (such as fuel additives) and will not be dealt here as they are not found or recycled in secondary lead plants. The kind of intake route, the size of the particle and the type of lead compound (organic or inorganic), dictate, together with the concentration and possible diffusion of the metal throughout the body. Beside these considerations, the lead absorption depends on other individual characteristics such as physiological 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.

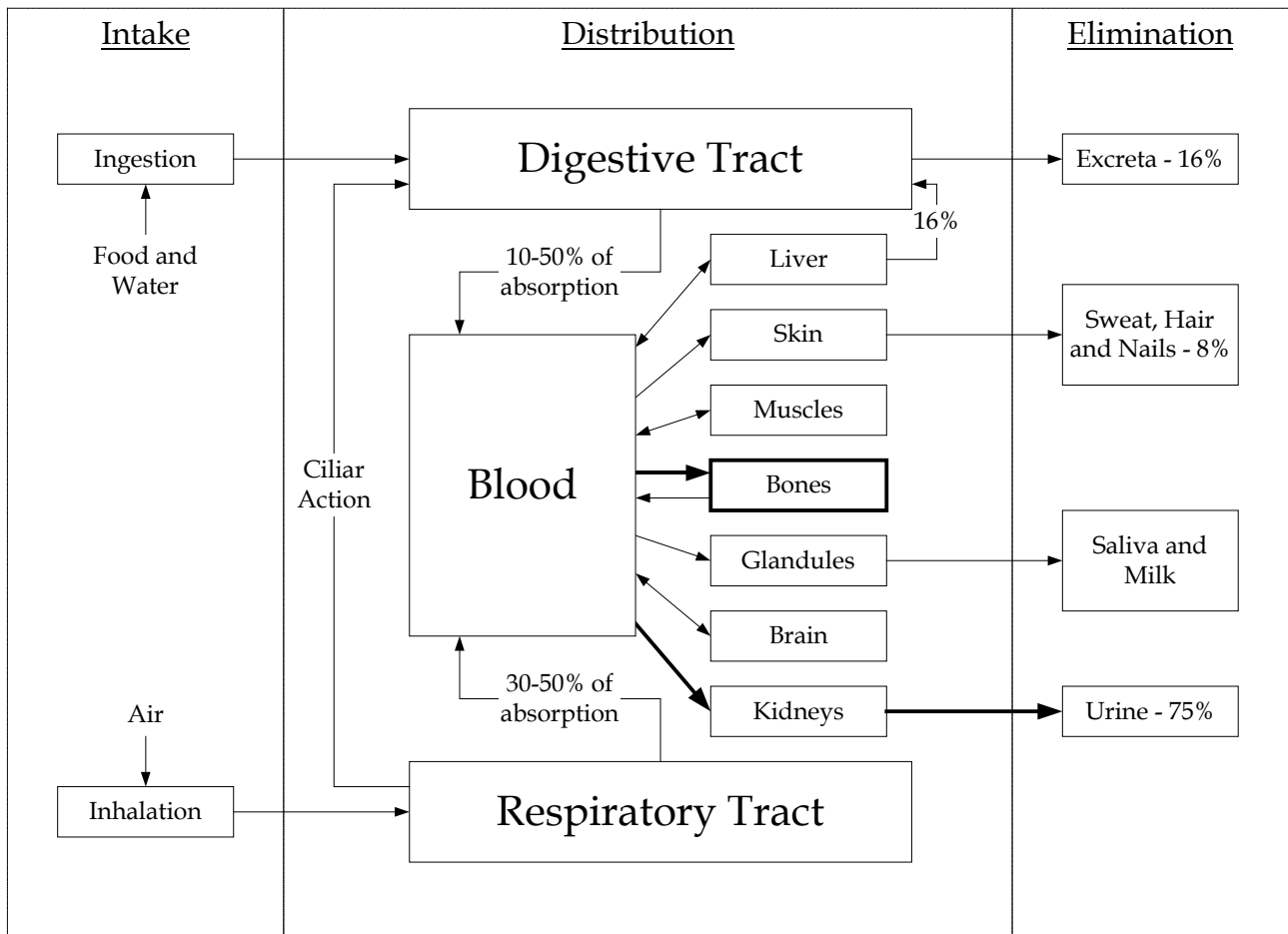


Figure 9: Toxicokinetics of lead in the human body

117. The inhalation route is the main source of lead absorption in the industrial 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 $1-2\mu\text{g.dl}^{-1}$ in the blood stream.

118. The gastrointestinal absorption, which is the main non-industrial 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 for other metal compounds, are the most extensively absorbed in the case of lead compounds.

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

120. The absorbed lead, both inhaled and ingested, is 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, especially bones which may retain around 90% of the body's lead content. Therefore, while the blood lead concentration reflects the recent exposure, bone lead concentration reflects the cumulative exposure.

121. The elimination of the ingested lead is mainly through the 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 eliminate lead through their milk in a concentration very similar to the plasma.

122. The half-life of lead compounds in the human body is, as a general rule, 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*

123. 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 dysfunctional and reflecting badly in several metabolic paths; (c) and by altering the transport of essential ions throughout the body.

124. A wide range of heterogeneous 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 young 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.

125. 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*

126. 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 often 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 (for example – smoking);

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

127. 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.

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

Table 1: Occupational lead exposure limits

129. 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)	< 30	30-40	40-60	> 60

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

6.3.2. Environmental Limits

130. 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, they are different from the occupational exposure limits that were extensively studied. The environmental limits still need further studies, consequently 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.

131. 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*

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

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

6.4.2. *Proposed Medical Control*

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

- (a) general health history of the patient;
- (b) occupational history in order to identify other exposures;
- (c) personal history of blood and nutritional diseases;
- (d) neurological history;
- (e) report on the medical examination prior to admission by the employee;
- (f) complete blood count;
- (g) determination of blood lead, ALA-U and ZnPP;
- (h) renal examination and tests;
- (i) electrocardiogram in order to evaluate the cardiac functions;

(j) special attention should be given to those workers who smoke and drink or are also exposed to other hazardous or toxic agents.

134. It must be stressed that the above procedures, not only the proposed actions for prevention and control, but also the proposed medical controls, 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.

135. With the above data it is possible, therefore, to establish the temporary incapacity of a worker who shows intoxication signs, provided that an appropriate counseling program is available to advise the worker of the best way to reduce his or her lead exposure levels.

6.4.3. *Periodicity of Control*

136. 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:

- (a) general working conditions;
- (b) toxicity of the considered substance(s);
- (c) concentration of the substance(s) in the environment;
- (d) exposure intensity;
- (e) exposure frequency;
- (f) personal protection degree (i.e. usage of personal protection equipment);
- (g) 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.

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

7. MAKING IT WORK: KEY STEPS FOR THE IMPLEMENTATION OF LEAD RECYCLING PROGRAMS

7.1. Detecting and Defining Country Priorities

138. The determination of a country's priorities must be the first step toward the environmentally sound management of lead-acid battery waste. Depending on the country's situation regarding waste management and raw materials, the best solution may be initially classified as one of the following:

(a) external recycling - lead-acid battery wastes will be collected and temporarily stored within the country and then exported to be recycled in other country;

(b) internal recycling – lead-acid battery wastes will be collected, transported and recycled within the country;

(c) regional solutions – a regional or sub-regional agreement is adopted in order to address lead-acid battery waste management making the most effective use of local or regional resources and expertise.

9. Notwithstanding this, once the country has recognized its priorities, the solution that best fits its needs may rely on two or more of the above options. For example, a densely populated country with some remote areas may adopt a scheme in which the battery waste is transported from the remote areas to the recycling facilities that may be located in the urban populated areas. Such a scheme may benefit from the advantages of both external and internal recycling strategies. Such adaptations however need a very precise diagnostic analysis of the country's position regarding the management of its waste materials, specially the cost advantages of lead recycling activities, since it is of utmost importance for the recycling process to be economically attractive.

7.1.1. External Recycling

10. This is the option chosen when recycling environmentally sound facilities are not available in the country or if a country is geographically so widespread, such as in an archipelago, that it is uneconomic to set up small recycling units. In this case, strategies should be adopted with the emphasis on the collection and transportation network with a convergence to the storage facility or facilities. Storage places should be strategically located in order to facilitate the loading of vehicles responsible for the transboundary movements of the used lead acid batteries, taking into consideration the technical guidelines previously outlined for storing and transporting.

7.1.2. Internal Recycling

11. Those countries that have environmentally sound recycling facilities installed and operating in their territory, will need to adopt strategies and policies in order to provide a legal framework to the collection, transportation and recycling of the used lead acid batteries. Policy frameworks and economic incentives may vary depending on the country's objectives, priorities and management goals for lead acid battery waste.

7.1.3. Regional Solutions

12. When two or more countries in a regional context do not have adequate or environmentally sound recycling facilities or perhaps one or more has and the other one or most of the others do not, a regional solution could be arranged. An example of this kind of action is the program currently under consideration in the Caribbean and Central America where several countries in this region expressed concern about the environmental consequences of the sound management of spent lead-acid batteries at the national level and sub-regional level.

13. The region consists of a relatively large number of small countries with small domestic markets for vehicle and industrial lead-acid batteries. Virtually all consumed batteries are imported as manufactured products, but at the end of their life they are discarded and are a hazardous waste subject to restrictive trade and environmental regulations. Although the Basel Convention encourages the domestic management of hazardous wastes and the minimization of transboundary movements, the small size of domestic markets will not support the setting up and operation of a viable domestic recycling facilities in every country. Therefore, a regional approach to this problem where resources are shared and the economies of scale are maximized is the most sustainable and therefore the best alternative.

14. The outcome of such programs should be:

(a) the development of national strategies for the environmentally sound management of lead acid batteries incorporated into a regional strategy which incorporates the development of policy tools and economic instruments;

(b) the definition of requirements and standards for an enhanced regional co-operative program or protocol for the environmentally sound management of these wastes;

(c) the creation of conditions where information, technologies and experiences could be shared between the regional members;

(d) the development of policy and economic measures in order to address any unregulated recyclers operating in the “informal” sector of secondary lead recovery.

7.2. Setting Collection Systems: Policy Frameworks

15. The technical aspects of the pre-recycling steps described previously under item 3 of these Guidelines, comprising collection, transportation and storage, must all fall under a policy framework capable of identifying players, responsibilities and economic incentives in order to give them long-term viability. This policy framework is required to:

(a) reduce waste generation

(b) provide means to:

(i) research the prolongation of battery lifetime;

(ii) research the use of alternative battery technologies;

(iii) the adoption of clean recycling technologies;

- (c) maximize economic and environmentally friendly lead recovery by means of:
 - (i) making recycling operations environmentally sound, economically efficient and socially acceptable;
 - (ii) including short and medium term measures for improving the efficiency of small smelters;
 - (iii) gradual insertion of the informal sector into a national lead recycling strategy;
 - (iv) increasing collection volume and reducing its costs;
 - (v) enhancing the access to domestic lead sources;
- (d) consider the strategy implementation as a consultative and multi-stakeholder process.

16. Some important procedures for the implementation of collection systems are:

- (a) as a basic premise, the participation of the consumers is the cornerstone for the implementation of all programs. Therefore, consumers should be informed about the fact that lead acid batteries are recyclable, what the procedures are for returning the used battery to the retailer, how the used batteries are stored while waiting to be dispatched to the collection center, and where the collections centers are located;
- (b) environmentally unsound destinations should be prohibited;
- (c) retailers should be licensed to collect and temporarily store used lead acid batteries, provided they have appropriate storage places in line with these technical guidelines. A minimum set of characteristics, relevant to each country, could be defined through legislation and further steps to encourage and enforce (if necessary) the implementation of such environmental protection, such as regular inspections of storage premises, should be undertaken. The licensing process should be viewed as a resource and the information used to publish a map of the collection network;
- (d) smelters should be licensed and adopt the best available technologies if they are to be installed, or modify their processes and/or operating practices in order to achieve high standards of environmental protection. Permanent control of emissions is also recommended;
- (e) resource sharing in consortia could be viewed as a solution to budget constraints since these arrangements decrease the cost of operations. If pertinent, a set of rules to regulate these associations could be implemented.

17. Several models for the implementation of collection systems were developed around the world in order to achieve specific country needs, taking into consideration country size, available transport network, local taxes, etc, and it seems to be a general trend to develop legislation based on the principle of producer responsibility. Some of these models are described below, in order of increasing complexity.

7.2.1 Simplified Reverse-Distribution System

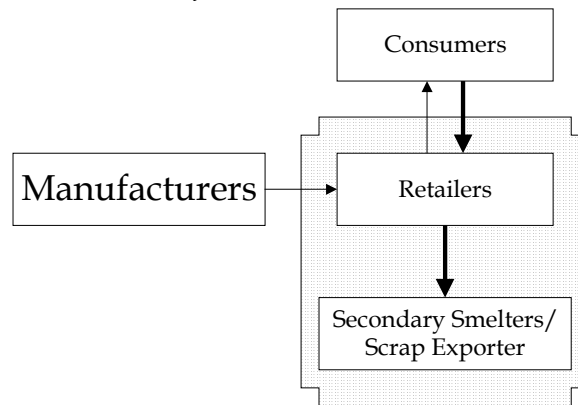


Figure 10 – Simplified reverse-distribution system

18. This is the simplest model possible under the scheme of the “reverse-distribution system” developed by some countries and is better suited for small countries or islands where the secondary smelter is rather close to the collection centers. The key idea of this system is that retailers are the collection centers for used batteries and, in the process of exchanging the old used battery, the consumer leaves the old one at the retailers where it will be properly stored until it can be transported to the smelter. In this model, the smelter’s role may be undertaken by the scrap exporter if the country chooses to export its used batteries instead of licensing a recycling facility.

19. Since this system uses the premise that retailers are in direct contact with the smelter/exporter, the geographic area covered by this scenario should be small. A general consequence of implementing this system is the lack of transport infrastructure, which is present in the next system, and would certainly poses some serious problems when the geographic area to be covered is quite large⁴.

20. Some important regulatory points are:

(a) transportation standards should be implemented in order to make the rather “informal” transportation network environmentally sound;

(b) if there is no licensed smelter and the scrap exporter is the conduit for effective recycling, then the exporter should not only be licensed and achieve high standards of environmental protection in any storage facility (which could be quite long time depending on the battery demand), but also should present a detailed set of operating procedures describing its activities and those of its partners in other countries in order to facilitate governmental actions in the regional scenario.

⁴ Of course “large” is rather subjective in this case, and a diagnosis should be carried out in order to determine if the sellers can carry out their activities without being overwhelmed by distances, taxes or other constrains. It may also be implemented as sub-regional answer.

7.2.2 Collectors System

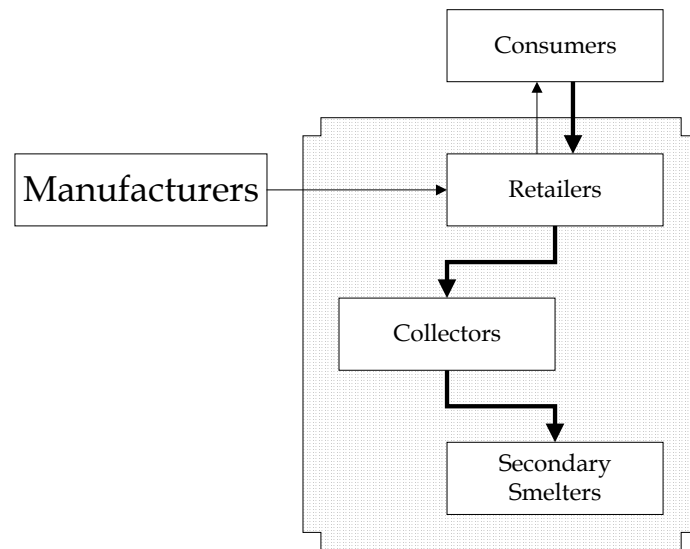


Figure 11 – Collectors system

21. Based on the models implemented in England and Germany, this system relies on the fact that, after the collection of used lead-acid batteries by the retailers, they will use a specialized collectors network that will take them to the smelters. Differently from the above described system, in this one the role played by the collectors ensure that the transportation costs will not be taken completely by the retailers. Besides, due to the increasing specialization of the activities, higher environmental standards may be achieved in the transport process. The main legislative step in this system is the control of the collection and transportation network and those players involved.

22. Due to the higher number of players in this system, its implementation allows for a wider geographical area to be attended, suggesting that medium sized countries could benefit from it. Notwithstanding this, based on the acumen normally shown by the retailers, this system could be also implemented in small countries and islands without major changes to its structure.

7.2.3. Manufacturer Supported Returning System

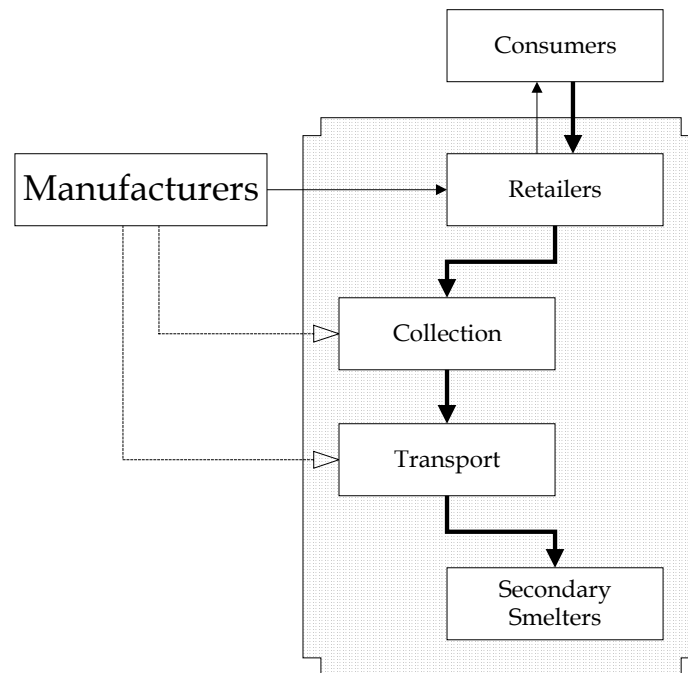


Figure 12 - Manufacturer supported returning system

23. Similar to the systems implemented in Japan and Brazil, this system foresees that the battery manufacturers will be indirectly responsible for the collection and transportation of used lead-acid batteries. This system differs from the above described in three ways:

- (a) the manufacturers will be responsible for planning and implementing the logistics of returning the used batteries so that they can be delivered to the secondary smelters;
- (b) there are two different players for the collection and transportation of used lead-acid batteries;
- (c) the collectors and those responsible for the transportation are linked to the manufacturers.

24. In this way, despite the fact that the manufacturers are not directly involved with the collection and transportation of the used lead-acid batteries, it remains their responsibility to provide the necessary means in order to accomplish these steps to a high environmental standard.

25. The manufacturer's supported returning system is ideally implemented in countries where a strong, but rather undisciplined and/or unregulated, collecting network is already present. Such a logical step means that everyone benefits by formalizing a somewhat unorganized infrastructure by providing a legal framework for it so that it is possible to identify those involved and their responsibilities.

7.2.4. Reverse-Distribution System

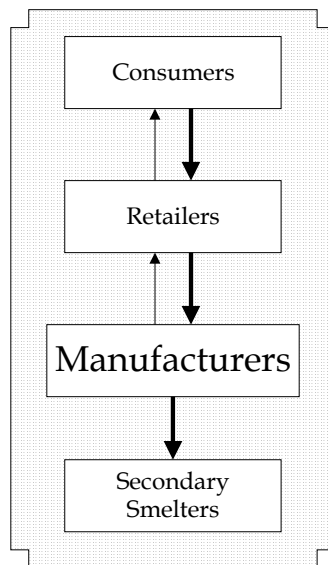


Figure 13 – Reverse-distribution system

26. Based on the French and United States system, this model is the complete reverse-distribution system, in which the manufacturers are directly linked with the collection and transportation steps.

27. This could be viewed as the most controlled collecting system. A very restrictive legal framework could be planned in order to provide complete coverage of all steps in the recycling chain. An educational and environmental program is also a necessary step to this program to be effective.

7.3. Improving Communication

28. Despite the importance of the lead recycling processes, they are usually regarded as a potential source of environmental contamination and population lead exposure. Accordingly, secondary lead plants are often regarded with suspicion by the surrounding community. This phenomenon can occur even when a company adopts the highest possible standards of environmental protection if it fails to communicate its high standards of environmental performance to the community and the workforce. Any mistrust between a responsible recycler and the local community can be addressed through effective community outreach programs.

29. Any dialogue and communication in a community outreach project should be open and honest, especially in the assessment and resolution of any issues. This principle should apply no matter how unsatisfactory the situation might appear to be, so that credibility is maintained, respect is earned and trust is forthcoming.

30. Any population working in or living close to a secondary lead plant is susceptible to lead exposure as is the environment. It is clear therefore that the objectives of any outreach project must include a community care program and regular environmental and biological monitoring so that the implications of any adverse results are understood and the appropriate action taken. It is also essential that education features strongly in the outreach agenda.

31. As a first step towards a community engagement it is important to identify common concerns and interests to facilitate and build working relationships. The most likely issues of common interest will be:

- (a) population health and safety, in and outside the workplace, including childhood lead exposure;
- (b) environmental protection, in particular waste management including effluent treatment and the disposal of any solid residues;
- (c) measures that promote a viable business and sustainable employment.

32. Responsibilities for coordinating reporting in those areas of common interest should be shared equally between the community and company representatives, bearing in mind that it is essential for everyone to work in partnership and help each other. To provide feedback to the Company's senior management and those members of the community not actively involved in an outreach program it is important for all decisions and discussions to be properly distributed. To do this:

- (a) establish records and make a briefing note of all meetings, decisions and any forthcoming actions that will either impact on the Company or the community;
- (b) publish data, information and meeting minutes in the public domain;
- (c) ensure that there is independent auditing of environmental and occupational exposures, both in the community and the company through prestigious organizations such as local Universities or other expert bodies.

33. Above all in order to make a valued and lasting contribution to any community engagement project those involved must:

- (a) know and understand the key issues, the technology, the health effects of lead exposure, the communities' social needs and priorities, government agendas and the economic factors affecting the recycling business;
- (b) do not walk away from problems, no matter how insoluble they seem to be, instead get the background information, anticipate the likely problems and solicit the help of other experts in the field and local interested parties in order to resolve them;
- (c) share your concerns and expertise freely to improve understanding;
- (d) above all it is important that rules are applied at meetings so that listening is paramount and that everybody involved is sensitive to the needs of the community and the recycling plant.

34. Key success factors that have been identified from case studies are:

- (a) stakeholders are committed to and identify with the projects' agreed objectives;
- (b) communications are honest, open, frank and frequent;

(c) objectives are realistic and agreed by all the stakeholders with action focused firmly on achieving and maintaining the aims of the program;

(d) responsibilities for each aspect of the program are clearly defined and ownership discussed and agreed;

(e) population health and local environmental goals are based on sound management, constructive dialogue and agreed action so that any achievements made can be sustained.

8. LEAD-ACID BATTERY AND LEAD STATISTICAL DATA

8.1. Primary Lead

8.1.1. *Primary Lead: World Concentrate Production*

Table 4: World mine production of lead concentrates, 1998-1999

	Mine Production (thousands of tons)	
	1998	1999
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	3080	3020

8.1.2. *Primary Lead: World Metallic Lead Production*

Table 5: World primary lead production, 1998-1999

	Primary Lead Production (thousands of tons)	
	1998	1999
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	2890	3010

8.1.3. *Primary Lead: World Metallic Lead Consumption*

Table 6: Metallic lead consumption by continents, 1996-1999

	Annual Totals (thousands of tons)			
	1996	1997	1998	1999
Europe	1942	1968	1952	1999
Africa	120	121	132	127
America	2056	2085	2177	2245
Asia	1795	1770	1673	1810
Oceania	74	70	64	64
Total	5987	6014	5998	6245

8.1.4. Primary Lead: Uses of Metallic Lead

35. Battery manufacture is by far the largest single end user 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, 1999

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

36. While there is a wide regional variation on the battery share, on the 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, 1993

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

8.2. Secondary Lead

8.2.1. Secondary Lead Production

Table 9: World secondary lead production, 1999

	Secondary Lead Production (thousands of tons)	
	1998	1999
USA	1120	1110
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	2880	2810

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

37. 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 and Tobago and Ukraine.

Table 10: Percentage of secondary lead production, 1999

	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	1110	1460	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	3010	2810	5820	48,3

8.3. Lead-Acid Batteries

8.3.1. *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

8.3.2. *Lead-Acid Batteries: Uses*

Table 12: Uses of lead-acid batteries (% of global market), 1995

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

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

- (a) size and characteristics of the vehicle population;
- (b) vehicle production and number of batteries per vehicle;
- (c) average battery lifetime;
- (d) behaviour 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), 1995

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

8.3.3. Lead-Acid Batteries :Lifetime

(e) 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, 1995

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

8.3.4. Lead-Acid Batteries: Composition

(f) 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

9. FINAL CONSIDERATIONS

(g) 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 others, which is out of the scope of this technical guidelines.

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

(a) 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;

(b) 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;

(c) international standards, such as ISO 14000 series, should be pursued;

(d) the formulation and adoption of specific regulations and mechanisms such as ecolabels should be studied as important factors;

(e) 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.

(i) 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
 - 1.1.1. *Geographical features*
 - 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

- 2.1. General aspects
- 2.2. Environmental protection investments
- 2.3. Environmental impacts at operation phase
 - 2.3.1. *Liquid effluents*
 - 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*
 - 2.5.3. *Control measures*
 - 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*
 - 2.6.5. *Control measures*
 - 2.6.6. *Conclusions*

- 2.7. Solid, liquid and pasty wastes
 - 2.7.1. *Waste identification and quantification*
 - 2.7.2. *Waste storage*
 - 2.7.3. *Possible effects of generated wastes*
- 2.8. Odors
- 2.9. noise pollution
 - 2.9.1. *Noise source identification*
 - 2.9.2. *Control Measures*
 - 2.9.3. *Conclusions*
- 2.10. Movements
 - 2.10.1. *Raw materials*
 - 2.10.2. *Products*
 - 2.10.3. *Wastes*
 - 2.10.4. *Conclusion*

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

1. It must be taken into consideration that since lead is a naturally occurring metal its presence in the human body is inevitable, and the normal range of blood lead levels is $10\text{-}40\mu\text{g.dl}^{-1}$. Evidence of harmful effects in adults is rarely seen at blood concentrations below $80\mu\text{g.dl}^{-1}$ 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.

2. 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 resulting in elevated levels of free erythrocyte protoporphyrins (FEP).

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

4. 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.

5. 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 them 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.

6. 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 from lead poisoning and a considerable proportion of these 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: δ -aminolevulinic acid
ALA-D: δ -aminolevulinic acid dehydratase
ALA-U: δ -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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Chapter 2 – Technical Data on Lead-Acid Batteries

- Various Sources. For a comprehensive overview consult: “Recyclage de batteries plomb-acide et environnement – Rapport Technique n.° 14”, Programme des Nations Unies pour L’Environnement, PNUE, 1998, 165 pp.

Chapter 3 – Lead-Acid Battery Recycling – Pre-Recycling Steps

- “Integrated Pollution Prevention and Control (IPPC), Reference Document on Best Available Techniques in the Non Ferrous Metals Industries”, European IPPC Bureau, May 2000, 807 pp.
- “The Recycling of Non-Ferrous Metals”, M.E. Henstock, an International Council on Metals and the Environment (ICME) Publication, MIM, 1996, 340pp.

Chapter 4 – Lead-Acid Battery Recycling

- “Integrated Pollution Prevention and Control (IPPC), Reference Document on Best Available Techniques in the Non Ferrous Metals Industries”, European IPPC Bureau, May 2000, 807 pp.
- “Recyclage de batteries plomb-acide et environnement – Rapport Technique n.° 14”, Programme des Nations Unies pour L’Environnement, PNUE, 1998, 165 pp.
- “The Recycling of Non-Ferrous Metals”, M.E.Henstock, an International Council on Metals and the Environment (ICME) Publication, MIM, 1996, 340pp.

Chapter 5 – Environmental Control

- “Integrated Pollution Prevention and Control (IPPC), Reference Document on Best Available Techniques in the Non Ferrous Metals Industries”, European IPPC Bureau, May 2000, 807 pp.
- “Lead, Mercury, Cadmium and Arsenic in the Environment – Scope 31”, Edited by T.C. Hutchinson & K.M. Meema, Scientific Committee on Problems of the Environment (SCOPE), International Council of Scientific Unions (ICSU), John Wiley & Sons, 1987, 360 pp.
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- ILMC Tool Box Series 1.2 - Control and Monitoring of Atmospheric Emissions, January 2002, Section 2, Emission Control Principles.

Chapter 6 – Health Aspects

- “Assessment of Human Exposure to Lead and Cadmium Through Biological Monitoring”, Edited by Marie Vahter, National Swedish Institute of Environmental Medicine & Department of Environmental Hygiene Karolinska Institute, Division of Environmental Health, WHO, Stockholm 1982, 136 pp.
- “Environmental Hazards of Heavy Metals: Summary Evaluation of Lead, Cadmium and Mercury – A General Report (1980)”, J.K. Piotrowski & D.O. Coleman, Global Environmental Monitoring System Programme Activity Centre, UNEP, Nairobi & The Monitoring and Assessment Research Centre (MARC), Chelsea College, University of London, 1980, 43 pp.
- “Lead in the Environment and Its Significance to Man – A Report of an Inter-Departmental Working Group on Heavy Metals, Pollution Paper No. 2”, Department of the Environment, Central Unit on Environmental Pollution, London, 1976, 47 pp.
- “Límites de Exposición Profesional a los Metales Pesados que se Recomiendan por Razones de Salud – Informe de un Grupo de Estudio de la OMS”, Organización Mundial de la Salud, Serie Informes Técnicos 647, WHO, 1980, 126 pp.
- “Serie Vigilancia 8 – PLOMO”, Germán Corey O. & Luiz A.C. Galvão, Centro Panamericano de Ecología Humana Y Salud – PAHO/WHO, Mexico City, 1989, 103 pp.

Chapter 8 – Lead-Acid Battery and Lead Statistical Data

Various sources:

- ILMC: International Lead Management Center;
- ILZSG: International Lead and Zinc Study Group;
- FAO: Food and Agriculture Organization;
- LDAI: Lead Development Association International;
- USGS: United States Geological Survey;

Annex 1 - EIA: Suggested Structure

- “Recyclage de batteries plomb-acide et environnement – Rapport Technique n.º 14”, Programme des Nations Unies pour L’Environnement, PNUE, 1998, pp. 122-124.

Annex 2 - Lead Poisoning Symptoms

- “Environmental Hazards of Heavy Metals: Summary Evaluation of Lead, Cadmium and Mercury – A General Report (1980)”, J.K. Piotrowski & D.O. Coleman, Global Environmental Monitoring System Programme Activity Centre, UNEP, Nairobi & The Monitoring and Assessment Research Centre (MARC), Chelsea College, University of London, 1980, 43 pp.
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The Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and Their Disposal (1989) is a global international treaty on hazardous and other wastes. The Convention sets rules for controlling the transboundary movements and disposal of hazardous and other wastes.

The main goal of the Convention is to protect human health and the environment from the adverse effect which may result from the handling, transportation and disposal of hazardous and other wastes. To achieve this, the Convention pursues three objectives: to reduce transboundary movements of hazardous and other wastes to a minimum consistent with their environmentally sound management; to treat and dispose of such wastes as close as possible to their source of generation; and to minimize both their quantity and hazardousness which is defined in the Convention as taking all practicable steps to ensure that hazardous wastes or other wastes are managed in a manner which will protect human health and the environment against the adverse effects which may result from such wastes.

The Basel Convention entered into force in 1992.

The Protocol on Liability and Compensation for Damage resulting from Transboundary Movements of Hazardous Wastes and Their Disposal was adopted at the fifth meeting of the Conference of the Parties in 1999, in accordance with Article 12 of the Basel Convention.

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