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United Nations Environment Programme  
*Industry and Environment*

**UNEP IE**

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# **Environmental and Technological Issues related to Lead-Acid Battery Recycling**

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**A Workbook for Trainers**

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Recycling**

*A Workbook for Trainers*

*First Edition • April 1996*



UNEP

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## Environmental and Technological Issues related to

# Lead-Acid Battery Recycling

## *A Workbook for Trainers*

This workbook is one of a series that provides practical support material to teachers and trainers wishing to commence or enrich their curriculum with up-to-date approaches in environmental management.

It is based on extended experience with training workshops by UNEP and other agencies, and is now being made available for wider use in all regions throughout the world.

### Acknowledgements

The first version of this trainers workbook was prepared in 1994 by J.W. Scheijgrond and F. Balkau for UNEP IE.

It was subsequently trialled in workshops and courses in several places, leading to subsequent revisions to produce this current document.

UNEP would like to thank the many individuals and organizations who contributed ideas and materials, or who assisted in reviews and redrafting. Particular thanks go to Mr H. Ahmadzai, Mr R. Boehnke, Mr J. Delcambre, Mr J. Hay, Mr M. Hyman, Mr M. Ichimura, the International Lead Zinc Organization Inc., Metaleurop (Mr P. Fossi, Mr P. David, and Ms E. Perrier), and Mr A. Tay.

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# Evaluation Form

## *Environmental and Technological Issues related to Lead-Acid Battery Recycling*

**A**s part of the continuing review of this trainers package, we would appreciate your cooperation in answering the following questions. Please return the completed evaluation form to:

UNEP IE, Tour Mirabeau, 39-43 quai André Citroën, 75739 Paris Cedex 15, France  
Fax 33 (1) 44 37 14 74.

- 1 Do you have any suggestions for improvement of the trainers package? How could we improve its readability, contents, practical use, and so on?

- 2 How was the package useful in preparing your own training activity?

- 3 Did the background information and the transparency set in *Part 3* provide you with enough information? What was missing?

*continued ...*

- 4 What resource information in *Part 4* was useful to you? What else should be included?

- 5 What are your experiences with the exercises in *Part 5*? What worked, and what didn't?

- 6 Do you have training material which could be incorporated into this workbook?

- 7 What additional topics related to cleaner production would you want to be included in the final version of this workbook?

*Thank you for taking the time to complete this evaluation form. Please return the completed form to  
UNEP IE, Tour Mirabeau, 39-43 quai André Citroën, 75739 Paris Cedex 15, France.*



# Users Guide

This is a trainers support package, *not* a reference book. It does not give a systematic, comprehensive overview (there is not enough room to do this); rather, it focuses on some selected aspects that are central to the subject. The structure of the document allows further sections to be easily developed and added as additional modules.

The package is written for trainers to provide them with support material and ideas, rather than as a study book for students. The average trainee will only ever see a few pages or exercises reproduced from this document.

One of the purposes of this package is to provide some case studies and situation scenarios that can be used as a basis for interactive training and simulated decision-making. However, the exercises only explore a small part of the potential of the case studies, and trainers are strongly encouraged to develop further exercises or tasks.

The package is oriented at developing insights and decision-making skills. For teaching the factual knowledge base of the subject, trainers are referred to the reading lists in the bibliography.

Work exercises are predominantly based on interactive groupwork and a team approach to

problem-solving. Such work needs to be guided by a tutor who is a recognized expert in the field. This method allows the full complexity of real decision-making to be explored.

Where calculations are required, they are more oriented towards throwing light on useful approaches or management decisions than simply finding the 'correct' answer. Trainers are strongly urged not to see this package merely as a set of arithmetic exercises.

In some instances, answers are indicated. For many problems, the 'correct' answer depends on the context of the question. It is here that a tutor or external resource expert is useful.

Many trainers find this disturbing. They should remember that real decision-making depends on the wider circumstances surrounding the problem, and that a numerical answer which is politically or socially unacceptable, or administratively unworkable (even though accurate), is not in effect 'correct'.

The simulation of real life situations and decision-making that is the basis of this package makes it most suitable for senior students and trainees, and especially for professional training (or retraining) courses.

Do not forget to refer also to the package on *Cleaner Production* for teaching the underlying concepts and approaches in this workbook.

Finally, we must stress again that this package does not cover all aspects of the subject. Its prime purpose is to lead trainers into this field, and to help and encourage them to develop their own material, appropriately tailored to their specific learning situation. UNEP is prepared to work further with trainers who wish to extend this package into new directions, or go into greater depths on some subjects.



## How to start a training activity based on this workbook

**1** *Remember that this is a starters kit*, not a complete recipe book. Remember also that the workbook aims to develop insights and decision-making skills, not to convey knowledge or facts. This is the task of the references listed separately.

**2** *Understand the needs of your trainees*. What insights or skills do you intend to develop? Define your learning objectives.

**3** *Refresh your memory* by reading some of the background papers and studying the overhead transparencies. Write your own notes in the spaces provided.

**4** *Identify some expert resource persons* who could be invited as tutors to help you in discussion sessions.

**5** *Select some of the exercises* you wish to present to trainees.

**6** *Examine carefully the case study or scenario* on which they are based. Be sure that you have at least one solution to the exercise that you can explain and defend.

**7** *Develop other exercises* or questions yourself.

**8** *Develop your own local case study* if you can, and use this instead of the one in the package.

**9** *Prepare some background questions* and preliminary exercises for trainees to carry out before they start the workshop/course.

**10** *In session, summarize the issues* for trainees using the overheads given, and others you may have. Discuss the problems and difficulties decision-makers face. Discuss where factual information can be found to help in decision-making.

**11** *Commence the work sessions*, preferably in small groups, and preferably guided by

a tutor. Discuss and compare results. Be open to ideas and experiences from trainees, and discuss these.

**12** *Return to the learning objectives*, and check that they have been achieved.

**13** *Consider how to follow up* and reinforce the learning experience by establishing some ongoing projects, or periodic reunions.

*Refer also to other packages and workbooks, where useful additional teaching material is found.*

To facilitate using this workbook, the header of odd-numbered pages describes the contents of that particular section. This information is also repeated in the footer of even-numbered pages. You can track your progress through the workbook by referring to the calibrations on the bar across the bottom of odd-numbered pages:

The shading shows your current position in the text.

# Glossary

This glossary contains some of the terms found in the background papers or in other papers concerning lead-acid battery recycling. This glossary is not complete and you may want to add further items.

*The following sources have been used: Environment Canada, UNEP IE, Greenpeace, and The Environmental Glossary (D. Dooley, K. Patrick)*

**APELL** *Awareness and Preparedness for Emergencies at a Local Level.*

**Bag filter** Name of a type of filter used for extracting airborne dust from the atmosphere.

**Basel Convention** *The Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and their Disposal (1989)* aims to control the transboundary movement and disposal of hazardous wastes.

**Battery breaker** A preliminary processor of batteries that applies a variety of techniques to break the battery, drain the sulphuric acid from the battery cavity, remove plastic and sell the lead components to the smelter. Battery breakers may be independent businesses or encompassed in secondary smelting operations.

**Cleaner production** The continuous application of an integrated preventive strategy to processes and products, in order to reduce environmental risks and impacts.

**Cradle-to-grave** The life cycle of a product, from raw material to final disposal.

**Dross** By-product which is formed during refining. Chemical compounds added during refining form drosses, which usually float on the molten surface. Apart from lead, drosses contain impurities such as copper, nickel, and antimony.

**Emission** An emission usually refers to fugitive or waste discharges from a process. Emissions are traditionally associated with atmospheric discharges.

**End-of-pipe treatment** Treating pollutants at the end of a process (by, for example, filters, catalysts and scrubbers) instead of preventing their occurrence.

**Environmental auditing** The management tool comprising a systematic, documented, periodic and objective evaluation of how well environmental organization, management and equipment are

performing with the aim of helping to safeguard the environment by: (i) facilitating management control of environmental practices; and (ii) assessing compliance with company policies, which would include regulatory requirements.

**Environmental impact assessment** An analysis to determine whether an action or project would significantly affect the environment.

**Good housekeeping** Efficient management of the property and equipment of an institution or organization. In the context of cleaner production, it often refers to the procedures applied in the operation of a production process.

**Grid** Metallic grille-like structural framework in a battery. Its purpose is to support the active material and conduct current to the cell terminals. It is cast from a high purity lead alloyed with approximately 5% to 12% antimony, 0.5% tin, and a few hundredths per cent of copper and arsenic.

**Heavy metals** Metallic elements with high atomic weights, e.g. mercury, chromium, cadmium, arsenic, and lead.

**Ingotting** Solidifying of lead in molds after refining.

**Lead bullion** The liquid lead, still containing impurities, which is formed in the smelter.

**Life cycle** The combination of processes needed by a product to fulfil the function specified by the functional unit. Life cycle stages include production, use and processing after disposal, including the processing of the waste generated in these stages.

**Life cycle analysis** A quantitative assessment of the total environmental impacts caused by a particular process or product, from resource consumption to contamination, from the cradle to the grave.

**Mass/Material balance** A precise account of all the inputs and outputs of a process, based on the law of conservation of mass.



- Matte** Molten material in the course of the recovery process in a smelter: it is not completely pure metal and requires further processing.
- Ore** A mixture of minerals and a gangue from which at least one of the minerals can be extracted at a profit.
- Paste** The mixture of lead oxide and lead sulphate, originating from the lead-acid batteries.
- Pollution** The term describes the presence of harmful, hazardous or detrimental constituents in an environment. A polluted environment describes a state that occurs when the assimilative capacity of the environment is exceeded, resulting in undesirable ecological changes.
- Primary lead purification** Originating from ores or concentrates. High temperature process where lead oxide drosses are reduced to metallic lead and impurities, such as iron, arsenic, antimony, and tin are removed in slags.
- Raw material** A material on which a particular manufacturing process is carried out.
- Reclamation recycling** The recovery of useful products from waste materials. The retrieval of materials or products for re-use in their original form or for reprocessing into other products.
- Recovery** The extraction of material from waste that may be recycled or reused. Recovery may take place at the source of waste production or as a process during waste handling.
- Refining** Removing of metals which are not desired in the end product by adding reactants which form drosses with the unwanted metals. The drosses are then skimmed off.
- Reuse** Retrieval of material or products for its original purpose within the same site. In case of lead-acid batteries: ensuring that no battery is taken out of service until it can no longer be serviced and used. Reuse efforts presently focus on reconditioning and recharging batteries to extend their useful life.
- Scrap** Discarded material from manufacturing or processing or remnants after an article's useful life has run out. Lead scrap is of three types: whole battery scrap, industrial scrap (such as drosses), and other scrap (such as cable sheathings).
- Scrubber** Device for flue gas cleaning. If dust and gas collide or contact with water, they will become entrained or absorbed in the water and so easily controlled.
- Secondary lead** Lead which has been used for different applications for which it has no longer has a purpose, and which is to be recycled.
- Secondary lead smelter** The metallurgical process that remelts or refines lead ingots, or lead-containing scrap of various types, and produces lead compound which is further processed.
- Separator** PVC plates functioning as isolators to keep the anode and the cathode from direct electrical contact. It is porous enough to retain sulphuric acid and allow electric current to flow between the plates.
- Slag** Solid waste produced from a metallurgical furnace. It is predominantly non-metallic in composition.
- SLI battery** Starting Lighting and Ignition batteries. They are used in cars, trucks, and buses.
- Smelting** The partial recovery of metal in molten form. Smelting is required to recover the metal content and convert it to a form that is ready for refining.
- Sustainable development** Meeting the needs of the present generation without compromising the ability of future generations to meet their needs.
- Sweating** The process where the molten lead is separated from the various types of scrap containing both metallic and non-metallic impurities. The process is executed in a reverberatory furnace.
- Technology assessment** A study or evaluation to help understand the likely impact of the use of a new technology by an industry or society.
- Used lead-acid battery** A lead-acid battery that has been taken out of service because it is spent, due to temporary battery failure, discharge, car scrapping, etc. Used lead-acid batteries present an environmental and health threat when improperly disposed due to corrosiveness and potential toxicity of component parts.
- Wrecking** The process during which the battery is crushed into smaller fractions. The sulphuric acid is separated first after which, optionally, the crushed battery can be separated into the following fractions: lead grids, lead paste, polypropylene, PVC, and ebonite.



# *Part 1*

## **Introduction**

<i>1.1 This package.....</i>	<i>1:4</i>
<i>1.2 Contents of this package .....</i>	<i>1:5</i>



# 1 Introduction

**M**any teaching institutions and individual trainers have difficulty in following the rapid evolution of environmental issues that are relevant to their courses.

This is particularly true when teaching subjects such as pollution and environmental management. And yet it is important that new graduates have a good knowledge of issues in which they may eventually provide consulting services or policy advice to governments and industry.

The fact that development and environment are interrelated means that it is more vital than ever that:

- *all professionals have a basic environmental literacy that helps them to incorporate environmental priorities into their specialized work, whatever their profession;*
- *specialized environmental courses are relevant to today's environmental agenda.*

In 1993, in response to these findings, UNEP, WHO, and ILO jointly initiated the programme on Training Approaches for Environmental Management in Industry. The programme aims to enhance the capacity of national institutions to offer local training on topics concerned with the prevention of industrial pollution.

In this context, trainers' packages have been prepared on different areas of environmental management. These packages are intended to help educators and trainers to develop their own workshops or curricula, or to integrate some of the ideas and information into already existing teaching programmes.

*It is important to keep in mind that these training resource packages merely provide a first orientation to the topic.*

*In no way does the package constitute a 'course' in its own right.*

## 1.1 This package

This package is a workbook that complements the trainer's package on 'Cleaner Production'. For best results, both should be used together. In many cases, it would be useful to use the *Cleaner Production* material as an introduction to any curriculum-based material in this workbook.

The workbook is balanced between curriculum-based content (useful for technicians) and a more management systems approach (useful for supervisors and managers). In practice, both will be needed, and the trainer is urged to develop a

balanced curriculum in response to the needs of his/her audience. Any missing elements may be found in one of the other UNEP manuals, to be converted into training format based on the case studies and scenario included here.

Thus, the package is not static.

As feedback is received from users and technical specialists, the material will be modified and enriched.

Users are encouraged to report on their experiences in using this package, and to send in *suggestions for improvements*.

The package focuses on the environmental aspects of product recycling. It uses battery recycling to illustrate that product recycling can, if precautions are not taken, cause serious environmental and health problems. The reasons why it has been selected for this training resource package are that:

- recycling of lead-acid batteries and lead scrap has a history going back to the last century, and is well understood.
- compared to other recycling loops, the recycling of lead-acid batteries is fairly simple and effective. In many countries, more than 90% of all lead-acid batteries are recycled.
- although recycling is often regarded as being automatically environmentally friendly, this is not always true. Lead-acid battery smelting confirms this. Smelting and refining of lead-acid batteries involve considerable risks for humans and the environment when no adequate pollution control measures are provided. However, simple disposal of batteries also poses serious problems for the environment. Lead-acid battery recycling functions as a useful role-model for recycling practices in this training resource package.

This role-model function (and its associated environmental problems) can be used as an example of how a recycling scheme is set up, and

how environmental problems related to recycling can occur and be solved.

This training resource package considers the technologies of recycling the various constituents of the lead-acid battery. We refer to these technologies as *secondary lead smelters*. Health and safety, pollution control, and environmental impact are integrated in this consideration.

It is during secondary lead smelting that the most serious environmental problems occur. The background papers discuss various secondary lead smelting technologies, and the exercises in *Part 5* also focus mainly on these technologies.

In the context of this package, it is impossible to include all the information on lead-acid battery recycling technologies. Due to increasing pressure forcing (secondary) lead-smelters to comply with stringent environmental standards, many developments are going on in this field, and many new technologies are emerging.

UNEP IE plans to publish in 1996/97 a technical report that gives a more comprehensive and systematic overview. The trainer may thus want to update this package from time to time. *Part 4* gives some addresses where updates on the latest technologies can be found.

The package is suitable for a wide range of audiences who do not necessarily need a technical background in order to be able to understand the suggested reading and undertake



the exercises in *Part 5*. The package can also be used to prepare a presentation on lead-acid battery recycling and its environmental impacts. The background readings and the transparencies provide the necessary information for this purpose. It gives the trainer enough background material and tools to prepare a three to four hour workshop.

All parts of the package can be used for preparing such a workshop, although some of the exercises may be time consuming.

Thirdly, the package can function as a resource for teachers to include the topic in existing curricula for undergraduate students who have a technical background. *Part 4* of the package can be especially useful for this purpose.

## 12 Contents of this package

This package is conceived principally to help trainers prepare a seminar, workshop, or extended course. It is not a course per se.

The package contains:

- suggestions and hints for *effective training*;
- a *short background* to the subject, drawn from other existing publications;
- *overhead transparencies* to introduce and illustrate the main ideas;
- *case studies* and situation reports and scenarios drawn from actual experience;

- supplementary *technical information* to support some work exercises;
- *work exercises* and questions;
- *appendices* with further information about UNEP and its programmes.

Trainers are encouraged to extend the package by adding their own case studies and exercises, and expanding the subject coverage into new topics. For example, trainers in environmental health may wish to add some modules on occupational safety and ecotoxicity by building on the chemical information already presented.







## *Part 2*

# **Organizing Effective Training Activities**

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<b>2.2</b>	<b>Notes on interactive workshop organization .....</b>	<b>ii:4</b>
<b>2.3</b>	<b>Some ideas for more effective communication .....</b>	<b>ii:5</b>
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<b>2.5</b>	<b>Resource persons guide .....</b>	<b>ii:7</b>
<b>2.6</b>	<b>Suggestions for self study .....</b>	<b>ii:9</b>

# 2 Organizing Effective Training Activities

## 2.1 Introduction

**C**ommunication and organizational skills are just as important as a technical appreciation of the subject. Professional educators already understand this point, but teaching is a very individual matter, and interactive teaching can be very demanding on a busy person.

Here, we recall some of the key aspects of the learning process.

This text contains suggestions about:

- *how to ensure maximum effectiveness as a trainer*
- *how to organize effective training activities and presentations.*

We have provided this advice before consideration of the technical material, so that readers can remind themselves of the importance of the advice when choosing work exercises and training projects, later in this package.

*Adults learn best when they are actively engaged. They remember 20% of what they hear, 40% of what they see, and 80% of what they discover for themselves.*

Accordingly, this package relies on interactive teaching methods, using working exercises, case studies, and groupwork problem-solving, rather than on lecture format.

Interactive techniques are more complex to organize than simple lecture-giving, but they give better results. In particular, interactive methods are more likely to provide students with practical skills. This is important where skill development rather than factual knowledge is the objective. Lectures are better at providing factual knowledge than at developing skills.

For example, a workshop format is very effective in providing training on the effective use of management tools such as *Environmental Impact Assessment* (EIA), or audits. For high level environmental management, both knowledge and skills are required, so the appropriate mixture of techniques should be used.

The notes in this Part are based on the experiences of UNEP IE and WHO in organizing workshops and other training sessions.

Personal advice on how to be an effective trainer is also given by several experienced trainers, who all use interactive training approaches.



## 2.2 Notes on interactive workshop organization

### 2.2.1 Workshops

**W**orkshops provide a stimulating learning environment where people with a wide range of experiences and skills can join together to address practical problems beyond the ability of an individual to resolve.

Interactive workshops use a combination of several techniques to bring about a deeper and more pragmatic learning experience than is possible with a lecture-style format.

Workshops also provide excellent opportunities for exchanging personal experiences, problem-solving through panel sessions and direct consultations with experts, and discussing some of the complex situations which surround most environmental problems.

The UNEP/WHO workshop format incorporates the following elements:

- sending out pre-workshop reading material, with some simple exercises

- preparation of a country report by each participant before the workshop
- short introductory or overview lectures on key issues
- practical problem-solving work exercises on case studies
- feedback by experts and discussions on workshop exercises
- panel sessions (that is, question-answer dialogues) with experts
- individual study sessions, computer quizzes, and so on.
- structured oral presentations of country reports leading to a regional overview
- audiovisuals such as videos, films, and slides
- field visits where appropriate
- personal action planning by participants for follow-up activity.

### 2.2.2 Preparation

**S**essions need to be carefully prepared, with participants knowing in advance what they will do or see. A proforma report form for country reports gives a common format to these sessions. Country reports should also try to link the issues with other sessions.

*It cannot be overstressed how important it is that participants should be thoroughly prepared for the workshops, and that all the pre-workshop activities have been completed.*

### 2.2.3 Organization

**T**he organization of working group sessions also requires care. Groups should first meet informally, elect their own chairman, and then act as a permanent team in various workshop sessions. They are guided, but not instructed, by technical experts.

It is useful to finish the workshop by preparing personal action plans. Participants should develop and present their proposals for what they can initiate immediately on their return home. Such action includes:

- what they can achieve unassisted, *and*
- what else they could achieve if some assistance were available.

The role of resource experts as advisors is crucial. They should have sufficient experience to assist in all sessions and provide general advice on all subjects in workshops, discussion or panel sessions. They should not, however, dominate the workshops.

The five day format is ideal for covering all these requirements. If less than five days is taken, you can be sure that important issues will be left out. If more time is available, consider including social events and private study sessions, along with more extensive project work for the students.

## 2.3 Some ideas for more effective communication

If the training is to be successful, effective communication is essential – from recognition of the training need to the final evaluation of the event.

Without good communication, all manner of things can go wrong:

- the training is too early – or too late – to make any impact on performance
- trainees do not know what the training is about or what to expect
- the course is planned for a local public holiday
- trainees who are traditionally used to lectures are suddenly required to take part in discussion groups, which might feel alien to them.

Most of these issues can be anticipated and overcome by good communication between the course designers, writers, and event organizers and presenters on the one side, and the students and their organizations on the other.

Some simple communication considerations will help to improve outputs in training and avoid disasters.

### Before the learning event

*Find out:*

- how the learners have been taught in the past
- the real needs and situation of the learners
- whether the facilities are adequate for the envisaged training
- whether the training has the support of senior people
- how success will be measured.

*Make a project plan for the organizers, giving details of how the event will be organized. Send the plan to them, with details of the key dates and needs.*

### During the learning

- find out how relevant the topics are to the work situation of the participants
- start with the familiar oil can – not a video of an oil spill disaster
- communicate using topics, themes and issues in the local press
- store unanswered questions, and remember to answer them before the end
- keep notes for participants to bullet-point format
- ensure the participants keep notes for future reference – few read essays, or even articles
- if you are working in a foreign language, at least translate the slides.

### After the learning event

- always communicate your thanks and best wishes
- inform participants on follow-up study procedures, and how the instructor can help to analyze the evaluations and inform the organizers of the results
- communicate to colleagues the results of the training and what can be learned from these results.



## 2.4 Some personal suggestions for effective training

The following suggestions come from four teachers with long experience in training. They are all different in character, and therefore in teaching approaches. However, they all believe in an enthusiasm for the subject which is critical when teaching students.

### ***To be an effective educator/teacher:***

- Provide an enjoyable learning situation that expands all of the participants' network.
- Model courses and teaching styles on examples that you think are outstanding. Ask yourself about the qualities of a good instructor or a good course, and follow the answers you come up with.
- Allow the subject matter to be discussed and discovered by students – not hammered in.
- Make courses relevant and interesting by understanding your audience. Ask them what they already know, and then plan for their needs. Incorporate ideas from the group in the course.
- Remember that no amount of style will substitute for a lack of substance.

**Deborah Hanlon**, Environmental Scientist  
Office of Environmental Engineering  
and Technology Demonstration, US EPA

### ***The outstanding educator/teacher:***

- Is fully acquainted with, and believes in, the educational merit of the subject matter.
- Utilizes clear and graphic illustrations to inform and motivate the students to learn.
- Utilizes learning approaches including multi-media, projects, interviews, questionnaires, debates, and similar interactive approaches to ensure full involvement of the students.
- Reacts positively to all questions – there are no Stupid Questions, only Stupid Answers.
- Remembers that positive reinforcement is a better motivational approach than criticism.
- Is available for private discussions with individual students or groups of students.

**Don Huisingsh**, Environmental Consultant and Professor at  
Erasmus University in Rotterdam  
the Netherlands

### ***To be efficient ('doing things right'), and effective ('doing the right things'):***

- Think about helping people to learn, rather than teaching them.
- Seek learner feedback, and measure learning achieved with objective tests.
- Set learning time limits.
- Seek conscious and unconscious learning.
- Seek learning that endures, based on understanding and skills.

**Bob Boland**, Environmental Consultant, France

### ***The best educator/teacher:***

- Likes the learners, and has a true understanding of how they learn.
- Has the ability to communicate.
- Will change the training programme and the approach if necessary.
- Is still learning, and has recent applied experience of the subject being taught.
- Has the ability to organise events and to manage things.

**Colin Sutherland**, Educational Consultant, France

## 2.5 Resource persons guide

**A**s this package relies heavily on interactive groupwork sessions, here are some guidelines on how to be an effective resource person.

In a case study-based training approach, the resource person serves more as a:

- facilitator of the group learning process
- technical adviser as needed,  
*and a*
- catalyst of learning  
*rather than a:*
- lecturer
- story-teller  
*or*
- instructor.

Here are some guidelines on how to be an effective resource person.

**1** Be sure that you have *read and understood thoroughly* the participant's notes before you meet your group. There's nothing like being prepared and more familiar with the case study scenario than the participants are!

**2** Before every group work session, take time to visit your assigned meeting room and check the:

- **seating arrangements** There should be a large enough table surrounded by enough chairs for the participants and yourself
- **equipment and supplies** such as flipcharts, flipchart papers, marker pens, white/black board, board eraser, masking tape, transparency sheets, writing pads, ballpen/pencils, calculator, etc.
- **physical conditions of the room** There should be sufficient lighting, the room temperature should be comfortable, noise should be as low as possible, etc.

**3** During the initial group meeting, it is important to set an *informal and friendly atmosphere*. It is suggested that you:

- **introduce yourself**, preferably asking everyone to call you by your first name, and then let everybody introduce himself/herself in a similar manner. *Do not waste time stating positions*

*and respective organizations, etc.*, which should have been done on the first day anyway.

- then ask if the *objectives and purpose* of the exercise, which have been previously discussed in the plenary session, are clear to them.

Sample objectives are:

- identify and understand the options that SMEs can employ in their pollution prevention program
- evaluate the feasibility and suitability of these options in view of technical, environmental, financial, organizational, and social criteria and constraints.

It will be useful to know whether the majority of the group members have actually read the text provided, which states the background and the problem.

If they have not, then you will need to direct them to focus their attention first on what needs to be accomplished by the end of each part.

**4** If your group gets involved in diverse issues, try to steer them back on the right track by *asking relevant questions*, rather than telling them what to do.

**5** Give *technical assistance and supplementary information* as needed,



without ‘spoon-feeding’ the participants. However, do not lecture or dominate the group discussion process.

- 6** Although you need not stay with your group for 100% of the time, it is expected that you:
- *spend at least 80% of the time* with them during regular sessions. The crucial times are at the *beginning, middle*, and near the *end* of each groupwork session.
  - If they decide to work beyond the prescribed regular time, just make sure that they are on the right track; your presence during overtime is not mandatory, but voluntary.

**7** There will be *critical parts* during the identification of options, followed by technical, environmental, and economic evaluation, where your technical advice will be most needed by your group.

The best way to assist the participants is by giving only the advantages and disadvantages of the options in question. Let them weigh these pros and cons and decide for themselves whether to take or drop the option.

**8** If you encounter any question about the technical content of the material that you have not been briefed on, discuss it with the Team Leader and *agree on how to tackle the situation*. It may well be that the other resource

persons need to be duly advised on the particular question.

**9** See to it that you *compare notes, exchange hints*, and *share strategies* with other resource persons so that you can assist one another, as well as gauge your group’s progress in comparison with the others.

**10** If tension or heated argument arises among your group members, try your best (with a sense of humor) to *defuse* it.

**11** In the case of *absenteeism*, approach the person/persons in question and encourage them to participate.

**12** If one or two group members are dominating the discussions or doing all the work, intervene and *encourage everyone to get involved*. In order to do this effectively, you need to be attuned to your group’s ‘culture’ and trend of discussion.

**13** Although *division of labor* is a time saving group work strategy, you must ensure that it is not done to the extent that there is no peer learning and discussion occurring. It is counter-productive for group members to work individually on these exercises.

**14** The most productive, meaningful and fulfilling group work is when they get to accomplish what they have to do *as a team* – and have fun in the process!



## 2.6 Suggestions for self study

**A**lthough this package was designed to provide resources for trainers, the potential for self-study should not be ignored.

The package does not constitute a complete course on cleaner production in leather tanning, but can be seen as an introduction to be

supplemented by further reading and additional training materials listed in the Appendices, and perhaps by site visits and discussions with professionals.

The following approach is suggested for individual study.

- Read the *introduction*, but avoid any sections on organizing training events.
- Seek out the section containing *background papers* or *subject content*. Read through the whole section as narrative.
- Work through the pages offered to the trainer for *overhead projection*, and ensure you can relate the key points of each overhead to the text you have read.
- Look at the section on *exercises*. Identify those which lend themselves to individual work, and tackle them. Those exercises clearly constructed for teamwork, or requiring research, may not be appropriate.
- Refer back to the *narrative* text as and when you need to, to complete the exercises.
- Check your *answers* against those given in this resource pack. Where there are discrepancies, check through your own working to understand why the discrepancies appeared.
- Use the *Appendices* to plan your own further development.





*Part 3*

# Technical Background Papers

3.1	Introduction .....	iii:3
3.2	Introductory articles .....	iii:5
3.3	The recycling scheme of lead-acid batteries.....	iii:17
3.4	Secondary lead smelting.....	iii:25
3.5	Transparencies.....	iii:57



# 3 Technical Background Papers

## 3.1 Introduction

**S**ection 3.2 contains some articles which introduce readers to basic facts on lead-acid battery recycling. Section 3.5 contains some transparencies which can be used as visual aids when explaining the concepts and principles of lead-acid battery recycling.

The articles in Section 3.2 are selected from different documents, and may therefore show overlap here and there. The text preceding each article gives some editorial comments and explains why the specific article is included in the background reading.

When using these articles for general programmes, one should take their national origin into account. More detailed information can be found from the references.

The articles used in Part 3 are as follows:

### 3.2 Introductory articles

- |   |  |
|---|--|
| <p><b>3.2.1</b> 'Environmental agency closes down company after finding lead in human blood, cows' meat'. In: <i>International Environmental Reporter</i> [April 6, 1994].</p> <p><b>3.2.2</b> 'Potential environmental and occupational hazard from lead'. In: <i>Lead Astray: the poisonous lead battery waste trade</i>. Washington DC, USA: Greenpeace/Toxic Trade Publications [1994].</p> <p><b>3.2.3</b> 'Mechanisms for risk reduction of lead in the European Community'. In: <i>Risk Reduction Monograph No. 1 Lead: background and</i></p> | <p><i>national experience with reducing risk</i>. Paris, France: OECD [1993].</p> <p><b>3.2.4</b> 'Processing and technology'. In: <i>Risk Reduction Monograph No. 1 Lead: background and national experience with reducing risk</i>. Paris, France: OECD [1993].</p> <p><b>3.2.5</b> 'Fundamentals of battery manufacturing'. In: <i>UNEP Design Manual II: Pollution Control Facilities for Small Battery Plants</i>. Bangkok, Thailand: UNEP Regional Office for Asia and the Pacific [1983].</p> <p><b>3.2.6</b> 'Batteries'. In: see 3.2.4 above.</p> |
|---|--|

### 3.3 The recycling scheme of lead-acid batteries

- |   |   |
|---|---|
| <p><b>3.3.1</b> 'Recycling'. In: see 3.2.4 above.</p> <p><b>3.3.2</b> 'Current management practices for used lead-acid batteries in Canada'. In: <i>Guidelines for the Management of Used Lead-Acid</i></p> | <p><i>Batteries in Canada</i>. Quebec, Canada: Environment Canada, Hazardous Waste Division, Office of Waste Management [1993].</p> |
|---|---|

### 3.4 Secondary lead smelting

- |   |   |
|---|---|
| <p>3.4.1 'The technology of lead-acid battery recycling'. In: see 3.2.2 above.</p> <p>3.4.2 'World Directory: secondary lead plants'. In: <i>World Directory: Secondary Lead Plants</i>. London, England: International Lead and Zinc Study Group (ILZSG) [1994].</p> <p>3.4.3 'Secondary lead smelting'. In: <i>Guidelines for the Control of Emissions from the Non-Ferrous Metallurgical Industries</i>. United Nations Economic Commission for Europe [1979].</p> <p>3.4.4 'Low waste technology for reprocessing battery scrap'. In: <i>Productivity and Technology in the Metallurgical Industries</i>.</p> | <p>The Minerals, Metals &amp; Materials Society [1989].</p> <p>3.4.5 'Lead scrap processing in rotary furnaces'. In: <i>Conservation and Recycling Volume 10:2-3</i> [1987].</p> <p>3.4.6 'Lead smelting: occupational safety and health guidelines'. In: <i>Occupational Health and Safety Guidelines</i>. Washington DC, USA: The World Bank, Office of Environmental Affairs [1984].</p> <p>3.4.7 'Summary of the Basel Convention and its consequences for lead-acid battery recycling'. Compilation of press releases and decisions on the Basel Convention.</p> |
|---|---|

**T**he background reading starts with an article on the closure of a secondary lead smelter and an article focusing on the potential environment and occupational hazard of lead. The aim of these articles is to show that (lead-acid) battery recycling can have serious environmental impacts on the environment.

To emphasize the hazardous characteristics of lead, the article on the regulatory status of lead is incorporated.

The article on the processing and technology of lead production introduces the reader to the most important compound of lead-acid batteries: lead.

The next article explains the composition of batteries, to give an idea what we are talking about when referring to lead-acid batteries.

The last article of the introduction focuses on the demand of lead-acid batteries worldwide.

**I**n Section 3.3, the reader is introduced to the recycling scheme of lead-acid batteries. The Canadian experience in lead-acid batteries is used to explain how this recycling scheme is managed and where the associated environmental problems arise. The table with the summary of '3Rs' options for used batteries illustrates that, through a cleaner production approach, the number of lead-acid batteries being recycled can be minimized – and thus also, the pollution from smelting practices.

In addition to the Canadian experience, readers may want to add a background paper on their own national lead-acid battery recycling scheme.

**T**he third section of the background reading starts with recommendations to recycling facilities to improve environmental performance through a cleaner production approach. The following articles explain the current technologies and scale of lead recycling. The most current practices are highlighted.

Some of the more modern, and environmentally friendly technologies are not being addressed, because they are only used on a small scale. However, with tightening environmental regulations, they are becoming increasingly important. It is therefore recommended that you to keep informed about their developments. The articles describing specific recycling technologies serve to give a basic understanding of the process, and are not chosen to show preference for any specific type of lead-acid battery recycling facility. The trainer is encouraged to include articles on more modern technologies.

An article on occupational safety and health guidelines in secondary lead-smelters describes how, through cleaner production options, the health and environmental impacts of secondary lead-smelters can be minimised.

The last paper is a summary of the Basel convention, describing the general contents of the Convention and its implications for transboundary transportation of used lead-acid batteries.



## 3.2 Introductory articles

### 3.2.1 Environmental agency closes down company after finding lead in human blood, cows' meat

**T**his article may serve as a case-study to emphasize the environmental problems related to secondary lead smelting. It is included in the background papers to raise interest in the topic and set the scope for the rest of the background readings.

In: *International Environment Reporter*  
The Bureau of National Affairs, Inc.  
1231 25th Street, N.W.  
Washington, DC 20037

[April 6, 1994]

**BRAZIL**  
**RIO DE JANEIRO** – For the second time in three years, a São Paulo metal processing company in a farming community on the outskirts of São Paulo has been closed down by the state environmental agency for environmental contamination.

Fae Metals, which manufactures battery plates from scrap metals, was shut down on March 8 by CETESB (Companhia de Tecnologia de Saneamento Ambiental) four months after farmers in the area of the factory complained that factory pollution was killing their cows. Veterinarians said that the cows had died from lead poisoning and that their milk and meat had been contaminated.

CETESB inspected the land and water within 500 meters of the plant and found levels in plant roots 900 times those permitted. Additionally, concentrations of lead in a nearby stream were eight times greater than the permitted level, and sediment in the stream contained lead 250 times the permitted levels.

São Paulo state law 8468 of September 1976 prohibits emission of lead that raises concentrations to more than 0.1 milligram per liter of lead in "class 2" water. Class 2 water is water that has been treated or is used for irrigation.

Tests by the São Paulo state health agency on 25 people living in the area found an average of 35 micrograms of lead per milliliter of blood. The maximum level set by the World Health Organization is 30 micrograms per milliliter.

Fae company officials denied that their plant is the source of the pollution. Gilberto Fae, the company's environmental manager, told reporters March 8 that a recent environmental audit showed that the smokestack emissions were well within acceptable limits.

#### Lead From Company's Operations

**F**lavio Bezerra, CETESB's manager of control for the interior of São Paulo, told BNA March 25 that the lead pollution did not appear to originate from the company smokestack, but from inefficient operations of the company's five kilns, which permitted excessive gases to escape. Additionally, wind and rain had spread lead particles from materials stored around the factory site, he said.

While CETESB, as an agency, is concerned with pollution to land, air, and water, Bezerra noted that "the major problem now is that we found lead in the blood of the people living in the region."

The agency is negotiating with the metal processing company on steps that must be taken before the plant can reopen. CETESB will require a comprehensive plan that will set out a series of deadlines for the manufacturer to install new procedures and necessary equipment to bring the pollution down to legally permitted levels, Bezerra said.

"We are looking for a way to link the reopening of the plant not only to the recuperation of the area, but to the improvement of the health of the local population," he told BNA.

The actual decision to reopen the plant, however, lies in the hands of Edis Milare, São



Paulo State's secretary of environment. The plant will "only be opened if it is crystal clear that there will be no health risks," he said March 23.

The metal processing company will first be required to curb pollution of water and vegetation, said CETESB's Bezerra. The company will eventually have to decontaminate the soil, but Bezerra refused to set a deadline.

"If they were required to restore the soil now, they would have to close down," he said, noting the expense of such a decontamination operation. "The strategy is for them to stop pollution to the water and air and later to recuperate the soil."

Officials of the São Paulo state prosecutor's office have been interviewing local residents. One prosecutor, Marcos Antonio Librelo, said the

office has gathered enough evidence to file a civil case against the company for environmental damage and injury to crops, livestock, and humans.

Neighboring farmers of the metal processing factory have fought with the plant since 1980, when members of the region filed a legal action to try to keep the plant from starting up. The neighbors said that the company's operations in another region had caused substantial environmental damage.

They also claimed that CETESB had been negligent in granting the company the right to begin operations in the region.

A state district court, however, ruled against the neighbors and permitted the plant to start up.

*April 6, 1994: International Environmental Reporter*

### 3.2.2 Potential environmental and occupational hazard from lead

**T**his article focuses on the hazards of lead. Air emissions of lead particulates are the most important and most dangerous exposure route to humans and the environment. However, keep in mind that lead-acid battery recycling also produces other problematic wastes such as slags, sulphuric acid and waste water resulting from secondary lead smelting.

In: *Lead Astray: the poisonous lead battery waste trade*  
Greenpeace / Toxic Trade Publications  
Washington, DC

[1994]

**L**ead is one of the most pervasive and toxic of all environmental contaminants, and some of the more extreme of its wide range of pernicious effects have been recognised for at least two thousand years. Metabolic, neurological and neuropsychological disorders can result from acute or chronic exposure. Interference with calcium metabolism and transport across nerve endings is believed to be the principle mode of toxic action in cases of neurological effect. The mechanism causing other lead related illness are generally less well understood, but some may be due to the lead binding to carboxyl groups in amino acids.

The classic neurological symptoms of exposure to high levels of lead are encephalopathy in children and peripheral neurotoxicity in adults. The latter is characterised by the loss of muscle control at the extremities, causing foot and wrist drop. Motor nerve dysfunction has been measured at blood lead levels of 50-70µg/dL.

Lead interferes with haemoglobin production, resulting in anaemia. This has been reported at blood levels of 60-80µg/dL. It also causes irreversible damage to the nephrons of the kidney, leading to a gradual reduction in the efficiency of uric acid excretion. High blood levels during pregnancy are correlated with a higher frequency of stillbirths and miscarriages, and transplacental transport of lead can damage

the central nervous system of the foetus. There is no placental barrier to lead transport, and evidence suggests that foetal brain tissue is particularly sensitive to lead poisoning, so it is especially important for pregnant women to avoid exposure. Paternal blood levels are related to congenital malformations in children, with levels commonly found in some work places possibly being inimical to spermatogenesis. There is limited evidence that lead is also a carcinogen in humans, with cancers of the kidney being most strongly associated with exposure.

Organic and inorganic lead are less toxic to aquatic plants than mercury and copper, with acute/chronic effects generally appearing at media concentrations of 0.1-5mg/L. Some terrestrial plants can also accumulate high concentrations of lead without apparent ill effect.

Acute effects of lead poisoning are usually reported in aquatic invertebrates at concentrations of 0.1-10mg/L, although some species, including some polychaetes and isopods, are particularly resistant to lead intoxication.

Fish are more sensitive to lead than invertebrates, with Lethal Concentration (LC) 50 levels of between 0.5-10mg/L. Sub-lethal effects, such as severe spinal deformities, have been recorded in media concentrations of less than 119µg/L.



### 3.2.3 Mechanisms for risk reduction of lead in the European Community

**T**his article illustrates the various existing tools for interventions which are aimed at reducing the risks of lead exposure to humans and the environment, taking the European Community as an example. Each country has its own guidelines and norms. Check these regularly, and consider including an article addressing the guidelines and norms which have been developed in your country.

In: Risk Reduction Monograph No. 1 *Lead: background and national experience with reducing risk*

OECD

Paris, France

[1993]

**A**lthough the European Community published environmental programmes in 1973, 1977, and 1983, there were no explicit legal provisions for Community environmental actions prior to the Single European Act taking effect in 1987. Despite this fact, over 100 instruments (mostly directives for harmonizing environmental protection measures) for environmental protection were proposed by Member States from 1972 through 1986. Reflected in these instruments, as well as in those proposed after 1987, is a desire to control lead in the environment.

The European Community has issued directives regulating lead in products and across different environmental media and environmental sources. It is important to note that a directive is a legislative action that is addressed to Member States and may either contain very specific information or be narrative in nature. A directive often sets a deadline for the Member States to adopt the directive into their own countries' law; typically, however, a directive will contain specific information and will set a deadline on the order of three years. If a Member country fails to adopt the directive into law within the specified amount of time, then action may be taken against that Member in the European courts.

Legal realities compound the difficulty of achieving environmental protection across the twelve Member States of the European Community, for the Member States are at different stages of environmental control, with varied levels of environmental awareness and/or concern, and have distinct regulatory entities. In regulating lead and other environmental hazards, the European Community must simultaneously prevent Member States from adopting rules that

would inhibit trade within the community and limit the extent of weak and inadequate environmental policies.

The experience of developing a lead policy in the EC exemplifies this regulatory challenge. For example, the European Community has issued policies that establish allowable lead contents for leaded and unleaded gasoline and encourage the use and manufacture of unleaded gasoline. Several European Community countries have switched to unleaded gasoline, but in countries such as Spain and Portugal, unleaded gas is a rare commodity. Despite these types of problems, the European Community has assembled an amalgam of instruments designed to control lead in the environment.

#### Blood lead action levels

**I**n 1977, the European Community introduced a directive on biological screening of the population for lead [77/312/EEC] designed to identify and control sources of unacceptable lead exposure. Each Member State was required to survey blood lead levels of groups of at least 100 persons in urban areas (population greater than 500,000) and in areas where significant exposure might be expected. At least two campaigns were required in each sampling area within a period of four years. Reference blood lead levels adopted for the study were 20mg/dl for 50 per cent of a group, 30mg/dl for 90 per cent, and 35mg/dl for 98 per cent.

For most of the study populations, blood lead levels fell well within the reference values. However, a small number of areas were found in which reference values were exceeded and remedial measures were subsequently employed. A general decrease in population blood levels



with time was apparent in most populations studied.

#### Lead-based paint

**B**eginning in 1989, the European Community prohibited the use of lead carbonates and lead sulfates in paints intended for all purposes other than preservation work [89/677/EEC; Rea 1987].

#### Lead in gasoline

**B**eginning in 1987, the European Community limited lead levels in gasoline. No specific deadline is designated to the Member States for meeting standards, but a committee was developed to provide scientific and technical support for meeting the standards. The directive [82/210/EEC] sets the maximum permitted lead compound level of leaded gasoline at 0.15 grams lead per litre and defines unleaded gasoline as gasoline that contains less than 0.013 grams lead per litre (0.020 grams lead per litre applied in certain exceptional cases until 1991) [IRPTC/UNEP 1990].

#### Lead in drinking water

**B**eginning in 1977, the European Community under Directive 75/440/EEC established classifications (i.e. A1, A2, and A3) for surface waters to be used as drinking water. Treatment methodologies were proposed for each

classification with all sources having to meet a maximum lead level of 0.05 milligrams lead per litre [von Moltke 1987]. This directive was supplemented by another in 1981 [76/869/EEC] that recommended uniform methods of measurement and analysis for Member States. Effective in August of 1982, the Community maximum allowable lead concentration was established at 0.05 milligrams per litre [80/778/EEC] [von Moltke 1987].

#### Lead in sewage sludge

**T**he European Community has made concerted efforts to co-ordinate analysis of the treatment and use of sewage sludge among Member States. In July of 1989, standards [86/278/EEC] for sewage sludge used in agricultural applications became effective. The lead concentration limit for soils with pH levels ranging from 6 to 7 is 50 to 300mg/kg dry matter, while the limit for lead concentrations of substances in sewage sludge is 750 to 1200mg/kg and the annual limit for lead in sewage sludge applied to agriculture is 15kg/ha (based on a ten-year average). In addition to these standards, the directive established analysis and record keeping guidelines for the treatment and use of sewage sludge [IRPTC/UNEP 1990].

### Standards for environmental media and point source controls

**S**everal policies have been established within the European Community to protect shellfish areas, ground and surface waters, and bathing waters. In order to support shellfish communities, the European Community has designated (as necessary) coastal and brackish waters for protection and improvement [79/923/EEC]. Beginning in 1981, Member States were asked to implement pollution reduction programmes within six years to protect these areas from lead as well as other heavy metal pollutants. The directive was written to support shellfish communities rather than bolster human consumption of shellfish [IRPTC/UNEP 1990].

The European Community initiated efforts to protect exploitable ground water supplies in 1982 [80/68/EEC]. At this time, inventory and surveillance measures were established to assess the extent of direct and indirect discharge of heavy metal pollutants into underground water

sources [IRPTC/UNEP 1990]. Effective in January of 1988, these measures were extended to include inland, surface, territorial, and coastal waters [76/464/EEC] [IRPTC/UNEP 1990]. Direct discharge methods and other disposal methods that may lead to indirect discharges are subject to the authorization of the European Community. Pollution reduction programmes are also encouraged to co-ordinate the authorization process as well as the development of alternative control options [von Moltke 1987].

The quality of bathing water [76/160/EEC] is specifically designated to be raised or maintained over time for both health and amenity benefits. Several parameters, including lead concentrations in water, are used to determine the quality of the water. The European Commission has also adopted measures to specifically protect the Mediterranean Sea from ocean dumping [von Moltke 1987]. Programmes to co-ordinate ocean dumping



prevention and assessment were initiated in 1977 after the Barcelona Convention. Other additional policy measures have been proposed to restrict ocean dumping of lead by requiring permits on a case by case basis [von Moltke 1987].

Beginning in December of 1987, the limit for ambient air concentrations of lead in air (expressed as an annual average mean concentration) was set at  $2\mu\text{g}/\text{m}^3$  [82/884/EEC] [von Moltke 1987]. Member States that anticipate exceeding this level are required to notify the Commission and must implement measures to ensure no repeat exceedences.

In 1982, the European Community encouraged the exchange of air monitoring data within the community [82/459/EEC] [von Moltke 1987]. By doing so, the community established a framework for comprehensive ambient air monitoring efforts. Beginning in June of 1987, the information exchange was formalized and plants that emitted high levels of pollutants, including lead, were required to use the best available technology (BAT), except in cases where costs were prohibitively excessive [84/360/EEC] [von Moltke 1987].

The burning and refining of used oil contributes markedly to ambient air pollution. Recognizing this source of air pollution, the European Community has taken measures to encourage the safe collection and disposal of waste oil. Beginning in 1990, the discharge of waste oils to water and drainage systems, deposit or discharge to soil, uncontrolled discharge of residues from processing, or any processing which causes high air pollution levels is prohibited [75/439/EEC] [von Moltke 1987; IRPTC/UNEP 1990].

The use of chemicals in agricultural production may contribute to groundwater pollution, as well as ecological and human health risks. The European Community has established a committee to set maximum permissible levels for heavy metals (including lead) in fertilizer products [76/116/EEC] [von Moltke 1987]. To date, however, no standards have been set.

The European Community has also taken initiatives to control the storage, treatment, and disposal of toxic and dangerous waste. To produce or hold these wastes requires a permit within the European Community; whereas, the storage, treatment, and deposit of these wastes must be authorized [78/319/EEC]. Beginning in

1987, the European Community agreed to conform to the standards set forth by the UN Economic Commission for Europe. These standards include labelling, contractual, and safety requirements [85/469/EEC] [IRPTC/UNEP 1990; ILZSG 1989].

The European Commission has set feed standards to limit the exposure of livestock to lead. Maximum allowable lead contents were established for several products: straight feeding stuffs (10mg/kg); complete feeding stuffs (5mg/kg); complementary feeding stuffs (10mg/kg); mineral feeding stuffs (30mg/kg); and certain specified feeding stuffs (5 to 40mg/kg) [IRPTC/UNEP 1990].

#### Lead in products

To prevent product standards from hindering free trade, the European Community has taken steps to harmonize much of the quality standards and labelling standards for consumer products. As of 1988, the marketing of cosmetic products containing lead was prohibited (with the exception of capillary products containing lead acetate) [76/768/EEC] [IRPTC/UNEP 1990]. Beginning in 1987, no more than 20mg/kg lead may be contained in colouring markers and not more than 10mg/kg lead in antioxidants and emulsifiers used for food [IRPTC/UNEP 1990]. The maximum leaching rate for ceramic articles that can be filled is 4mg/l; for ceramic cookware the maximum leaching rate is 1.5mg/l. In addition to these standards, there is a proposal to restrict the maximum bioavailability resulting from children's use of toys to 0.7 $\mu\text{g}$  for lead [von Moltke 1987].

#### Recycling

A 1991 directive on batteries and accumulators containing dangerous substances [91/157/EEC] requires that Member States ensure that spent batteries containing more than 0.4 per cent lead by weight are collected and disposed of under controlled conditions. Specific requirements of the directive include marking of batteries to indicate metal content and need for separate collection, design of electrical appliances to enable ready removal of batteries and the organization of separate collection systems including, if necessary, the use of economic instruments such as deposit systems to encourage recycling.

**Education/labelling**

**B**eginning in June of 1988, paints, varnishes, printing inks, varnishes, and similar products that have one per cent weight associated with heavy metals (including lead), must be classified, packaged, and labelled according to European Commission standards [77/728/EEC] [IRPTC/UNEP 1990; von Moltke 1987].

**Occupational standards**

**B**eginning in December of 1983, the European Community designated 14 measures to control occupational exposure to lead. These measures provided the basis for

industrial programmes, requiring medical surveillance and providing workers with open access to medical results and knowledge of potential dangers in the workplace [80/1107/EEC] [IRPTC/UNEP 1990; von Moltke 1987]. In 1986, the European Community supplemented these basic measures with monitoring and analysis techniques, concentration limits for air ( $0.15\text{mg}/\text{m}^3$ ) and blood lead ( $70\mu\text{g}/\text{dl}$ ), and action levels for air ( $40\mu\text{g}/\text{m}^3$ ) and blood lead ( $40\mu\text{g}/\text{dl}$ ) [82/605/EEC] [ILZSG 1989; von Moltke 1987].



### 3.2.4 Processing and technology

This article introduces the reader to the technologies and processes which are used to produce refined lead. Both lead-bearing ores and secondary lead may serve as input to produce refined lead. Lead from used lead-acid batteries is the main raw material for secondary lead.

In: Risk Reduction Monograph No. 1 *Lead: background and national experience with reducing risk*

OECD

Paris, France

[1993]

**L**ead metal is produced through a series of process stages. The number of stages required to produce metal is dependent on the type of feed material (i.e. mined ore or scrap material). Lead-bearing ores must first be mined and then concentrated before being smelted and refined into lead and lead alloys. Prior to smelting and refining of lead-bearing scrap (batteries), the battery cases must be broken and the acid, plastic/ebonite and lead components separated. The lead content of some scrap, such as lead sheet, pipe or boat keels, is high enough to allow it to be directly refined or remelted for reuse.

#### Mining and concentrating

**T**he common minerals in lead ores are galena (PbS), cerussite (PbCO<sub>3</sub>) and anglesite (PbSO<sub>4</sub>). Galena is the most common mineral and is usually found with other sulphide ores – most frequently those of zinc, copper and silver. Ore bodies near the surface are mined by open pit methods, while those that occur at depth must be extracted. Ore is first drilled, then blasted, crushed and carried by trucks and/or conveyors to a mill. There the metal-bearing sulphides are finely ground, separated by froth flotation from waste (iron and minerals that are not metal-bearing), and concentrated into separator bulk lead, zinc and copper concentrates. The concentrates are often dried to a specific moisture content, then shipped for smelting. The lead content in concentrate typically ranges from 50-70 per cent. The waste material (tailings) is carried in slurry form for use as back-fill in the mine or for disposal in an on-site tailings pond where particulate matter settles out and the effluent can be monitored and/or treated if necessary.

Methods to minimize the risk of dusting or spillage of concentrates and tailings can involve ensuring that materials are moist and non-dusting, that the mechanical design of handling systems is used to minimize spillage and permit clean-up, and that old tailings sites can be rehabilitated through options such as flooding, covering with topsoil and/or vegetation, or converting to wetlands/wetcovers.

#### Smelting and refining

**L**ead-bearing concentrates or scrap must be metallurgically treated to separate lead metal from various impurities, such as sulphur and silicate minerals in concentrates, or sulphates, oxides and other metals in scrap.

To extract lead from concentrates requires the conversion of lead sulphide into lead oxide, and then the reduction of the oxide to metallic lead (bullion). The two traditional methods are the Imperial Smelting Process (ISP), which simultaneously processes lead and zinc ores and is energy-intensive, or the sinter and blast furnace process, which will be discussed further as it is the most commonly used method at present. Newer, more efficient direct-smelting technologies have been developed and implemented in recent years.

#### The conventional sinter and blast furnace process

**C**oncentrates are often pelletized to increase porosity. Then heat and oxygen are applied to drive off the sulphur, as SO<sub>2</sub>, leaving a sinter of lead metal, lead oxide and other metal oxides or silicates. The SO<sub>2</sub> off-gas is blown through a cooling and dust collection system before going to an adjacent plant, where it can be used to make sulphuric acid or other sulphur products. Lead oxide is then reduced to metallic lead (bullion) in

a blast furnace, while silicates and other impurities form a residual product called slag.

Lead recoveries in modern blast furnaces range from 97 to 99 per cent of the lead content in the feed [SRI 1983]. Some operations recover additional metal from the slag by passing it through a fuming furnace to oxidize and drive off lead and zinc, which can then be collected in the form of flue dust. The molten slag is tapped from the furnaces. It is either granulated and vitrified, by being subjected to a water spray, or cooled and solidified slowly by the air. The slag can then be stored in piles either on-site or in a designated landfill site, or it can be used for construction purposes such as in block form as rip rap for dams. Where slag is used in construction, leachability must be considered. Flue dusts are usually recycled back through the smelting process.

#### The direct smelting process

The direct smelting process skips the sintering stage described above. Within a single furnace/chamber it uses the exothermic sulphide-roasting reactions, with air to provide the heat requirements to convert PbS to PbO and then produce lead bullion and slag [SRI 1983]. This method has the potential to provide a cleaner working environment by reducing the possibility for vagrant emissions of lead oxide (fume). The SO<sub>2</sub> off-gas, dusts and slag are collected and treated in the same manner as described for the sinter-blast furnace process.

The evolving processes are the Kivcst (Russian design), Isasmelt (Australian), QSL (German) and TBRC/Kaldo (Swedish). There is also the Outokumpu Oy (Finnish) process, which has not

yet been constructed on a commercial scale for lead.

#### Refining

Lead bullion from the smelting stage is refined to remove remaining impurities and traces of other metallic elements, including precious metals, either by the electrolytic or pyrometallurgical process. In electrolytic refining the lead bullion is cast at the smelter into plates weighing several hundred kilograms, which serve as anodes. Thin sheets of pure lead are inserted into electrolytic tanks with the anodes to act as cathodes. The continuous application of electricity in the solution dissolves the anodes, while the pure lead is deposited on the cathodes. Impurities such as precious metals that settle in the tank are removed for further processing. The refined lead, up to 99.999 per cent purity, is then cast into slabs, called pigs, for market.

Pyrometallurgical refining is carried out in a series of large covered or semi-covered kettles. The molten lead is transferred from one kettle to the other by pumping, or by ladle and crane, and each impurity or precious metal is progressively removed from the lead. Some secondary and primary lead producers may also choose to remove or add various metals to produce alloys. The techniques vary with the types of impurities and by-product metals contained in the molten lead. Selective reagents are added to the lead under carefully controlled temperatures, and the different drosses, containing impurities, that collect on the surface are skimmed off. When all impurities have been removed or the proper alloy is obtained, the lead metal or alloy is cast into pigs. In most cases, drosses are processed to remove precious and other non-ferrous metals.



### 3.2.5 Fundamentals of battery manufacturing

**I**t is important to understand the fundamentals of battery manufacturing because the constituents will be recycled later on.

In: UNEP Design Manual II *Pollution Control Facilities for Small Battery Plants*  
 UNEP Regional Office for Asia and the Pacific  
 Bangkok, Thailand

[1983]

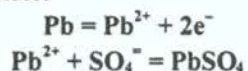
**T**he term *battery* refers to a device for converting chemical energy directly to electrical energy. Actually, there are “batteries” that do not depend upon a chemical reaction to produce electrical energy. Photovoltaic cells, for instance, convert solar energy directly to electrical energy and are called solar batteries. In this manual, the term battery will be limited to the familiar types of batteries, namely, the so-called dry cells used in flash-lights and lead-acid batteries used in automobiles. The term battery, strictly used, really means an assembly of two or more cells; but the term is now generally used to refer to one or more cells.

#### Lead-acid battery

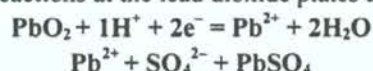
**A** storage battery is a connected group of two or more storage cells and the lead-acid battery commonly used in automobiles and motorcycles is the most common type.

The cycle of operation of a storage cell consists of: (i) charge, in which an electric current is passed through the cell to generate the chemical reactants within the well; (ii) standing, in which the energy remains stored in the form of chemicals while the cell is on open circuit; and (iii) discharge, in which these chemicals react on demand to produce an electric current.

The active constituents of a lead-acid cell are sulphuric acid, a set of plates containing lead and another set of plates containing lead dioxide. On discharge the lead atoms of the lead plates give up electrons and form lead ions, which in turn form lead sulfate:



The reactions at the lead dioxide plates are:



Charging a lead-acid battery reverses the chemical changes, displaces the sulfate from the plates and produces sulphuric acid.

#### Manufacturing of lead-acid battery

**T**he essential parts of a lead-storage battery are: the container, the positive electrodes or plates, the negative electrodes or plates, the insulation between the positive and negative plates, and the electrolyte. The manufacture begins with the casting of the grid on the plates. The grid is a metallic grille-like structure framework. It is cast from a high purity lead alloyed with approximately 5% to 12% antimony, 0.5% tin, and a few hundredths per cent of copper and arsenic. Antimony makes the grid hard and lead resists continued attack by sulphuric acid under storage battery conditions.

The grid is converted to a plate by filling it with active material in the form of a stiff paste that is made by mixing lead oxide with water and sulphuric acid in the proper amounts. The following reaction takes place:



Pastes for the negative plates are made with 75%-100% litharge (PbO) and 25%-0% lead powder or red lead in the dry mix. Expanders totalling less than 1.5% of the dry mix are added to the paste to provide better capacity, prevent loss of the spongy character of the negative-active material, and improve the operating characteristics during life. The expander is a mixture of barium sulfate, carbon black, and an organic material derived from lignin such as sulfonic acid derivatives.

For the positive plates, no expander is used. They are made from 65%-90% litharge, the remainder being lead or red lead. The manufacturing operations are the same as with the negative plates. Because of the absence of



carbon black, the positive plates are lighter in color than the negative plates.

The paste is forced into the interstices of the grid mechanically. After pasting, the plates are dried in drying ovens with proper humidity control at 38°-65°C for 12-15 hours.

After the plates have been pasted, dried, and assembled, they are immersed in weak sulphuric acid and charged. This process is called formation. Formation of the plates is necessary to convert the dried paste into the active electrode materials of the finished battery, namely, sponge lead in the negative plates and lead dioxide in the positive plate. Formation continues until the positive plates become dark brown, the negative

plates become metallic gray, the plates are gassing normally, and the voltages are constant and normal.

The positive and negative plates are kept from direct electrical contact by an insulator called a separator, which is porous enough to retain sulphuric acid and allow electric current to flow between the plates when carried by sulphuric acid. Materials used are: wood veneer, microporous threaded rubber, plastic or glass fibers.

The rest of the manufacturing process involves assembly into the plastic or rubber container, labelling, and packaging.

### 3.2.6 Batteries

This article gives an idea of the global production level of lead-acid batteries and an idea of how big the potential market for used lead-acid batteries is.

In: Risk Reduction Monograph No. 1 *Lead: background and national experience with reducing risk*

OECD

Paris, France

[1993]

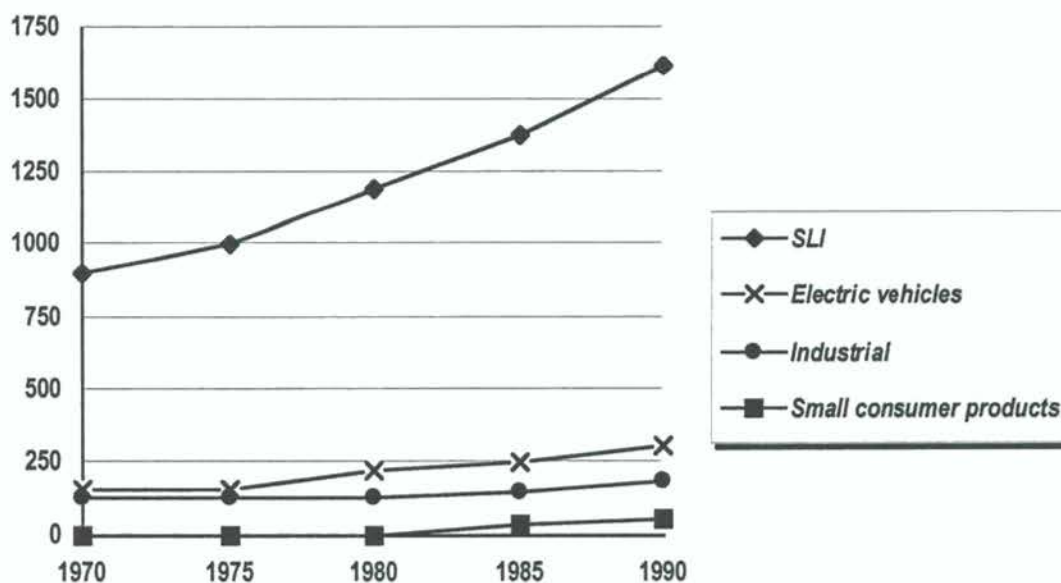
Since 1970, the battery sector's demand for lead has increased by 79 per cent to 2.12 million tonnes in 1990. *Figure 3.1* shows how lead demand has steadily increased over the last 20 years for all types of lead-acid batteries: starting, lighting and ignition (SLI), electric vehicle, industrial, and small consumer products.

SLI batteries, which are used in cars, trucks, buses, etc., accounted for 78 per cent of the battery market in 1990. Batteries to power electric vehicles, such as fork lift trucks, airport ground support vehicles, delivery vans and golf carts, were the second largest category at 14 per cent. The third largest category was industrial batteries, such as those used as stand-by power to

provide uninterruptible electrical energy supplies for telephone exchanges, public buildings, hospitals, submarines and various industries.

Lead oxides and alloys with antimony, calcium, etc., are used in the production of battery components such as paste, grids and posts. Other battery components include plastic or ebonite cases, separators and electrolyte (sulphuric acid). All components can be easily separated and either recycled, reused or safely disposed. Technology is available not only to neutralize the acids, but also to convert the sulphur for use in fertilizer or detergent products. The extent of application depends, of course, on the availability of markets for these products.

Figure 3.1 Batteries



SLI – to start, light and ignite cars, trucks, buses, boats, etc.

Source: LDA 1992, ILZSG 1992 a.



## 3.3 The recycling scheme of lead-acid batteries

### 3.3.1 Recycling

This article introduces the reader to lead recycling and the market for its product. Used lead-acid batteries account for over 63 per cent of world demand for lead.

In: Risk Reduction Monograph No. 1 *Lead: background and national experience with reducing risk*  
OECD  
Paris, France  
[1993]

Lead is one of the most recycled non-ferrous metals in the world. Annual production from recycled materials (i.e. secondary lead) has risen steadily. It exceeded primary output for the first time in 1989. Factors that influence lead recycling include type of product, historical demand levels, product life span, collection system infrastructure (including transportation), international trade, scrap separation and processing technologies, prices of scrap lead compared with lead metal, currency exchange rates, environmental regulations, and the return of spent products by consumers.

Technology is available to recover lead as well as other metals and materials (for example, plastics) from lead-bearing residues and waste. Lead-bearing feed for recycling can vary from industrial scrap (for example, plating or chemical solution/sludge, baghouse dusts, refining drosses, dirt residues from fragmentizer plants used for shredding steel cars, domestic appliances, etc.) to remediation and abatement wastes such as lead paint removal debris, lead-contaminated soil, and firing range soils. Post-consumer product scrap constitutes more than 80 per cent of the scrap supply for recycling (for example, batteries, cable sheathing, radiation and sound attenuation materials, sheeting, crystal glass, wheel weights, and electronic equipment, which also contains precious metals), with batteries accounting for up to 90 per cent of this amount in a given year.

Recycling rates are usually stated for batteries, as they account for over 60 per cent of world demand for lead. As for other recyclable lead products, recycling rates are not usually available since they tend to have variable life spans, which

makes it difficult to determine the amount of material available for recycling in a given year. shows battery recycling rates in some OECD countries.

Battery recycling rates are determined by comparing the amount of lead recycled from batteries with the quantity available for recycling, in a given year. Recycling facilities can usually provide data on the amount of lead produced from scrapped batteries. However, the amount of lead available for recycling is largely influenced by the battery's life span. Therefore, to determine the amount of lead available from batteries for recycling in a given year requires historical data on battery production and average lead content, as well as import and export data on new batteries and vehicles containing batteries. Also required are current data on the lead content of batteries in scrapped vehicles and import/export data on scrap lead, scrap batteries, and scrapped vehicles containing batteries. Methods of calculating recycling rates may vary by country, according to available data.

It should be noted that the average lead content in batteries has decreased over time because of technology changes. The life span can also vary depending on climatic conditions and energy demand requirements (for example, air conditioning, heaters). The average battery life for passenger vehicles is estimated at four years in the United States and three years in Japan.

As indicated in *Table 3.1*, battery recycling rates are high in many countries. This is largely because of the favourable economics associated with recycling batteries. However, it has become apparent that the weakest link in the recycling



chain is usually the consumer who discards a used battery rather than returning it for recycling. In a number of countries, governments are working with industry to increase recycling by focusing on the battery life cycle and persuading the consumer to return used batteries. Initiatives include: mandatory take-back requirements for retailers and manufacturers; requirement of a cash deposit if an old battery is not returned when

a new one is purchased; a small tax on new replacement batteries that can be used to offset the cost of transporting used batteries from remote regions; or a deposit/refund scheme by which consumers pay a deposit when purchasing a battery and are reimbursed when it is returned. It should be noted that the latter scheme could stimulate vehicle battery thefts if the cash deposit/refund were set too high.

**Table 3.1** Battery recycling rates in some OECD countries

	1986	1987	1988	1989	1990	1991
Australia						>90
Belgium	77					
Canada						93
France	80			90		90
Germany FR	83					>95
Italy	83					
Japan	93.3	92.5	95.2	93.8	92.2	
Norway						50 *
Spain	83					
Sweden						>100 *
United Kingdom	84					93
United States		88.6	91.0	95.3	97.8	

\* There are no lead recycling facilities in Norway.

Scrap batteries are collected and then exported to other countries for recycling.

e = estimated

Note:

Methods used to determine recycling rates may vary by country. Recycling rates can exceed 100 per cent when stored or stockpiled batteries are returned.

Sources:

Commonwealth Environment Protection Agency, Australia [1992]; Energy, Mines and Resources, Canada [1992]; Federal Environment Agency, Germany [1992]; State Pollution Control Authority, Norway [1992]; National Chemicals Inspectorate (KEMI), Sweden [1992]; US Bureau of Mines [1992]; US Department of Commerce [1992]; ILZSG 1991; Battery Council International (BCI) [1992].

### 3.3.2 Current management practices for used lead-acid batteries in Canada

The components of the recycling network for lead-acid batteries, from consumer to the secondary lead-smelter, may differ slightly from country to country. The case of Canada is chosen to give an example of such a network.

*Editorial comments:* In cadmium is listed as an additive. However, in Europe cadmium is replaced by copper, selenium, or arsenic. Cadmium forms toxic volatiles during smelting.

In: **Guidelines for the Management of Used Lead-Acid Batteries in Canada**  
Environment Canada, Hazardous Waste Division, Office of Waste Management  
Quebec, Canada

[1993]

#### Overview

In Canada, an informal network has evolved for managing the collection and recovery of used lead-acid batteries across the country. Because of the high potential of lead-acid batteries to be recycled, they tend to be regarded as a commodity and are subject to the same economic pressures as any other commodity. This network or system has operated well in most regions of Canada at times of high world lead prices. In other words the scrap value of the used lead acid battery is greater than the costs of collection, handling, storage and transport to the battery breaker.

The net effect of the world lead market on the Canadian recycling industry has been many periods of loss, followed by short periods of profit. Although price is certainly a significant determining factor as to whether a used lead-acid

battery enters the recycling system, there are also a number of other important influences. These include the regional distribution of batteries across Canada and variations in geography, as well as the characteristics of individual consumers and retailers. The implications of these factors are discussed in the following sections.

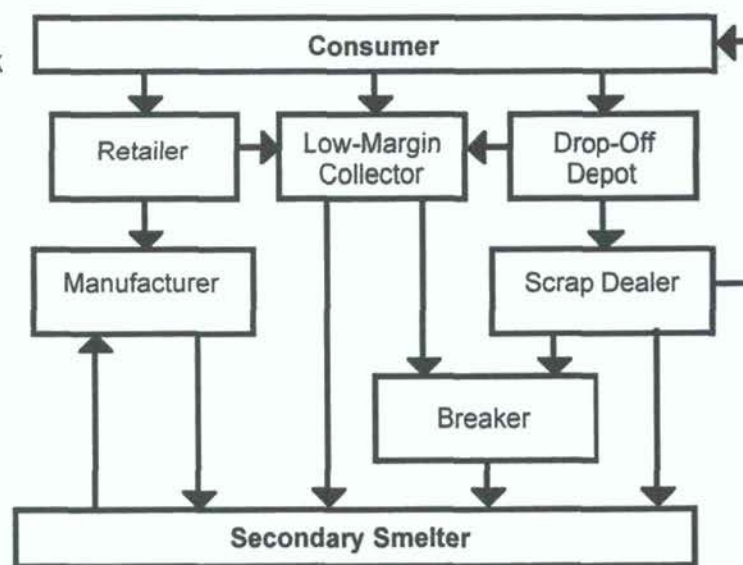
#### The used battery collection network

The used lead acid battery collection network in Canada can be described in terms of four general categories:

- the consumer
- the transportation network
- the battery breakers
- the smelting operations.

The relationship between these components is shown in *Figure 3.2*.

**Figure 3.2**  
Lead-acid battery recycling network





**The consumer**

**T**he battery collection network begins with the individual consumer or company who requires a replacement battery. The diversity in the sources and types of replacement batteries leads to many of the problems associated with the collection of the used batteries. If a consumer chooses a battery dealer or a service station, it is normal practice for the dealer or service station to keep the used battery. The used batteries are then accumulated until a battery wholesaler or a scrap dealer arranges to purchase or take them. However, if the individual consumer chooses to replace the battery themselves, return options are not as clear.

**The transportation network**

**T**raditionally, the used battery collection system has operated on the basis of small, independent, low-margin collectors (pedlars). For the most part, these operators collect used lead acid batteries in conjunction with other scrap materials. In this way, the collectors handle batteries as a commodity, just like other scrap such as steel or aluminum.

The transportation network also includes the dismantling of wrecked automobiles. Although a small proportion of these batteries are routed to 'reconditioners' where they are sold for reuse, the majority are routed to battery breakers.

In addition to the commodity market itself, transportation costs are a controlling factor with regard to the number of batteries that will reach a breaker in any given period. As a result the system tends to favour the batteries taken out of service in areas near breakers and has resulted in significant storage in areas away from breakers. Batteries in more remote areas tend to be 'stored' until lead prices rise to the level that will cover

both transportation and handling costs. If prices do not increase to acceptable levels there is the potential for inappropriate storage and/or disposal.

**The battery breaker**

**B**attery breakers are usually stand-alone operations although they have been increasingly absorbed in Secondary Smelter Operations. Battery breakers procure materials from scrap merchants. Breaking operations separate batteries into four distinct parts:

- the acid;
- the lead oxide/lead sulphate/lead plates;
- the plate separators, and;
- the plastic.

The acid that is recovered is either sold or used in subsequent processing. The plastic is sold in the plastic recycle market while the plates and separators are sent to smelting operations.

The prevailing world lead price also has a strong impact on the economic viability of battery breaking operations. When world prices are low, breaking operations are only marginal at best. This results in the greater potential for an operation to forego or delay changes which are necessary to meet environmental regulations or operational and maintenance needs.

**Secondary lead smelters**

**S**econdary smelters buy used lead from battery breakers or from scrap dealers, and re-smelt the metal (i.e. melt down and resell to the manufacturers as a raw material). The lead from all lead bearing materials of the battery, including the separators can be recovered in smelting operations. However, treating of the separators results in lower furnace life and longer smelting times, thus lowering efficiencies.

**Features of Canadian lead-acid battery management****Recycling**

**M**ost constituents of today's lead-acid batteries are recyclable and in fact, contribute to a relatively closed-loop recycling chain. For instance, lead is reprocessed and reused in battery manufacturing. Sulphuric acid is often reprocessed and used in manufacturing or added to fertilizer or other chemicals. Plastic

constituents can be cleaned and repelletized for further use in manufacturing battery cases or plastic moulding applications.

Several retailers and manufacturers of used lead-acid batteries now encourage and accept return of post-consumer lead-acid batteries. Every manufacturer surveyed as part of this project, has established a system to take back



used lead-acid batteries from any or each of assembly plants, wholesalers, distributors, major customers (i.e. large retailers), hospitals, warehouses, lift truck firms, manufacturers and schools. Those who have not yet established collection systems indicate that they are investigating the possibility of doing so. Therefore, it can be concluded that recycling of lead-acid batteries is becoming increasingly common in Canada.

Data supplied by Energy, Mines and Resources Canada [Smith 1992], for purposes of this study, provide insight to recycling rates in Canada. They are presented in *Table 3.2*. Making use of estimates generated previously, the results of applying the two different methods for determination of the amount of available SLI

batteries in Canada, can be compared to estimates of amounts processed by secondary smelters. The most obvious aspect of this table is that for 1991, the apparent Canadian recycling rate for lead-acid batteries is greater than 100 per cent. It is probable that the main reason for this somewhat anomalous number is that the recycling industry is drawing upon the significant amounts of batteries that are in inventory from previous years throughout Canada. This is particularly significant because world lead prices were depressed in 1991. Therefore the smelters or processors were probably only drawing upon localized portions of the residual inventory (i.e. within a geographically close area). The implication of this is that there are still significant amounts of batteries in remote areas that remain in inventory.

**Table 3.2** Canadian lead-acid battery recycling rate [1991]

<b>Estimated tonnage of (available) batteries</b>		
<i>Manufactured in Canada:</i>		
SLI auto & heavy duty	2,432,464	
Other SLI batteries	75,532	
Imports (SLI auto & heavy duty)	2,476,425	
Batteries contained in scrap vehicles	1,022,716	
<b>Total SLI batteries</b>	<b>6,007,137</b>	
<b>Total tonnes of SLI batteries (based on mass of 17.2 kg)</b>		<b>103,323</b>
<b>Estimated tonnage of (available) batteries (based on vehicle registrations)</b>		
Total vehicles registered	17,246,074	
Annualized estimate (assume 3.5 year average life span of battery)	4,927,450	
Batteries contained in scrap vehicles	1,022,716	
<b>Total SLI Batteries</b>	<b>5,950,166</b>	
<b>Total tonnes of SLI batteries (based on mass of 17.2 kg)</b>		<b>102,343</b>
<b>Recycled batteries (from Energy, Mines and Resources Canada research)</b>		
Tonnes of Canadian SLI batteries processed	91,000	
Batteries contained in scrap vehicles	21,000	
<b>Tonnes of Canadian SLI batteries recycled</b>	<b>112,000</b>	<b>112,000</b>

### Reuse

**B**attery reuse consists of recharging and 'reconditioning' batteries. In terms of automotive, SLI batteries, reconditioning is almost always restricted to recharging and subsequent sale of batteries salvaged from scrapped vehicles. This is a very small proportion

of the Canadian battery management system. Most consumers prefer to purchase a new battery.

Actual reconditioning of batteries is almost always restricted to large industrial batteries. Separator plates may be replaced, a portion of the sulphuric acid replenished and the battery recharged.

### Current fate of pollutants generated as a result of used lead-acid battery management

#### Components of lead-acid batteries

The major components of a lead-acid battery are the electrodes, electrolyte and casing.

The positive electrode (cathode) typically consists of pure lead dioxide, and the negative electrode (anode) a grid of metallic lead containing various elemental additives including antimony, arsenic, cadmium, copper and tin.

Table 3.3 indicates the type and proportions of constituents of lead-acid batteries, based

primarily on the lead-acid automotive battery. This information was provided by Energy, Mines and Resources Canada [Smith 1993], based on information on the recovered portions of SLI batteries and the lead recycling industry. The additives are used to increase anode hardness. The additives and their typical concentration ranges are shown in Table 3.4 [Basy et al 1991]

**Table 3.3**  
Constituents of used lead-acid batteries

Component	per cent weight
Metallic lead	17
Lead sulphate/oxide	50
Plastic	5
Acid	24
Residuals *	4
<b>Total</b>	<b>100</b>

\* Residuals refers to ebonite and separators.

**Table 3.5**  
Metal concentrations in lead-acid batteries

Metal	Concentration (mg/L)
Particulate lead	60 - 240
Lead (dissolved)	1 - 6
Arsenic	1 - 6
Antimony	20 - 175
Zinc	1 - 13.5
Tin	1 - 6
Calcium	5 - 20
Iron	20 - 150

**Table 3.4**  
Chemical additives to lead-acid batteries

Additive	Concentration (%)
Cadmium	0.1 - 0.14
Antimony	2.5 - 7.5
Arsenic	0.15
Tin	0.1 - 0.5
Copper	0.05

An average automotive battery weights 17.2 kg and contains about 9.0 kg of lead, equally divided between anode and cathode(s) [Basu et al 1991]. The electrolyte is generally 15 to 20 per cent sulphuric acid (pH = 0.8) and is known to contain dissolved and particulate metals released from the electrodes due to dissolution. Typical metal concentrations in lead-acid battery acid are shown in Table 3.5 [Watts 1984]. The additives are used to increase anode hardness. The additives and their typical concentrations ranges are shown in Table 3.4. At the time of manufacture, an automotive battery of 17.2 kg contains approximately 6 litres of sulphuric acid. The casing of an automotive battery weighs about 1.4 kg. Nowadays, the casing is constructed of polypropylene although hard rubber materials (e.g. ebonite) have been used in the past.



## 3.4 Secondary lead smelting

### 3.4.1 The technology of lead-acid battery recycling

This article gives the reader a short overview of the processes and technologies used to recycle lead-acid batteries. For a more detailed description of the technologies of battery recycling, see following background reading.

In: *Lead Astray: the poisonous lead battery waste trade*  
Greenpeace / Toxic Trade Publications  
Washington, DC

[1994]

#### Background

Lead has the highest recovery rate of any non-ferrous metal, with more than 50% of world demand met with recycled material. Over 60% of lead used in the OECD is consumed in lead acid batteries.

The history of recovery of lead from batteries in industrialised countries stems from small, privately-owned companies processing local waste, and the development of larger companies operating on a regional basis. Equipment was unsophisticated, and a unilateral approach to plant design was the rule. Prior to the 1960s, these operations were unrestricted by environmental and public health constraints, leading to operational problems for workers and environmental contamination. During the mid 1960's technological improvements improved efficiency, and reduced occupational and environmental hazard to some degree. Increasing environmental pressures, coupled with poor market conditions and lack of government strategy with regard to battery recycling caused the industry to decline during the 1980's, with many companies ceasing to trade. Those that survive have adopted a policy of non-expansive consolidation.

Lead recycling operations in developing nations have incurred costs because of the increasing environmental stringency demanded of industry in the West. Low wages and lax environmental standards and/or practise mean that a high margin of profit can be returned on secondary lead recycling in South America and South-East Asia.

Thus, industries have developed in many developing countries which resemble the lead

recovery operations of the West sixty years ago, in some instances with considerably lower standards on worker protection and environmental impact.

#### Processing and recycling

Lead scrap is of three types: whole battery scrap, industrial scrap (such as drosses and skimmings) and other scrap (such as cable sheathing). In the US in 1980, 71% of all scrap was obtained from used batteries, and it is likely that batteries form an even more predominant part of scrap today.

The environmental standards achieved by battery resmelters vary widely. The procedure adopted may be truncated or altered in different plants. For instance, the entire battery might be charged to the smelter without prior removal of the casing. OECD countries would therefore require an afterburner on the smelter to combust hydrocarbons in the exhaust, and scrubbing apparatus to remove sulphur dioxide and hydrochloric acid. Such expensive equipment is not likely to be installed in lead smelters in non-OECD countries, and will certainly be absent from "cottage" smelters.

Hazards are associated with all stages of the recycling. Storage of spent batteries can give rise to lead oxide dusts and runoff of acids into groundwater. In OECD countries, the storage yard would have a concrete base and a storage tank to collect runoff and a rain moisturizing system to prevent dust formation.

In OECD countries, batteries are handled by a closed cab, air-conditioned bulldozer, and then dumped directly into the crushing system.



Separation of plastic and lead-bearing material is handled by flotation, producing:

- 1) lead oxide in decanted slime
- 2) grid scraps or lead alloy containing antimony (1.5-6%), arsenic (0.15-0.2%) and tin
- 3) plastics, including PVC, polypropylene and rubber
- 4) liquid effluents, containing the battery acids and lead oxides.

#### **Inputs**

**F**inal refining occurs in large “kettles”, requiring considerable quantities of hygiene air to collect the fume and dust, so that very large filtration plants are needed to treat the volume of exhaust that arises.

Cable sheathing, weights, pipes and other high grade sources of scrap are fed straight into the smelter with no preparation, whilst lower grade scraps such as drosses and flue dusts from the smelting of lead and other non-ferrous metals are mixed with the charge before smelting. As with copper smelting, the primary and secondary processes are not always distinct. All primary smelters reintroduce the residues from flue dust into the furnaces, and many (e.g. the Avonmouth plant in Bristol) import such materials from other plants. The advantages of economy of scale and the difficulties in locating new smelters are leading to calls for increased integration of primary and secondary plants, including battery recycling units.

#### **Wastes**

**A**tmospheric pollution in the working environment and outside the plant is probably the most significant threat to human health caused by lead smelting. Elemental lead and lead oxide particles occur in workplace dusts, which are generated particularly in the furnace and ingotting departments. In addition, high concentrations of air borne antimony can develop, especially during refining and ingotting. These dusts are theoretically collected in bag filters and venturi scrubbers before air is discharged to the environment, and are fed back into the process. Significant sulphur dioxide emissions may also occur, especially if batteries are not crushed and separated before smelting. In addition, HCl fumes and products of incomplete combustion (PICs) may be produced. Water used during the process becomes highly polluted, and

must be treated before discharge. Water outflows arise from the following sources:

- a) water used in the crushing and separation phases, which contains sulphuric acid as well as lead oxides and salts;
- b) cooling waters for the ingot machine, contaminated with lead salts;
- c) waters used in the fume wet-cleaning process, which will contain all compounds located in the fume;
- d) waters used for yard irrigation, contaminated with leads and acids.

The waste water arising from these sources will require thorough neutralisation and flocculation/sedimentation of solids before discharge. The two other principal waste products are plastics and rubber from battery cases and slags. Some of the plastic can be recycled, but the rubber and slags are landfilled, possibly on site.

#### **Pollution-control technology relating to lead smelting**

**E**missions of lead and sulphur dioxide during pyrometallurgical processes are very difficult to control. However, expensive pollution abatement technologies can reduce human and environmental exposure. Of the £10 million recently spent by J H Enthoven & Sons on updating their secondary lead smelter in Derbyshire, UK, 40% was invested in pollution control.

The principle measures that are taken within conventional battery recycling plants in OECD countries to mitigate aerial pollution are:

- a) Irrigation of the storage yard, to prevent high levels of lead dust forming during dry weather. Contaminated water treatment involves neutralising acidity and removing suspended material. This is achieved by the application of lime, and the flocculation and decantation of solids, respectively. The sludges produced are some times dried and re-inserted into the recycling process.
- b) Mechanisation of all lead handling. In particular, the workers involved in breaking the used batteries before smelting are protected in plants like Enthoven & Sons in the UK, who use a crane, with a sealed and air conditioned cabin, to prevent contact with lead.



c) Air suction in all process departments, and the removal of particulates by bag filters. Careful design of the air extraction system is required to avoid the point furthest from the fan being starved of “pull”. This problem can be mitigated by the inclusion of small booster fans.

Lead smelting operations vary between those fitted with the best available technology for pollution abatement, (as most plants in OECD countries do); those having some technology for pollution abatement, but is either archaic or capable only of primary filtration or removal (such as some of the plants in South East Asia, reviewed below); and those having no pollution

abatement technology (such as “back street” or “home” smelters). Back street smelters comprise of small factories which rely on manual labour and crude technologies to break up and smelt lead battery waste. “Home” smelters consist smelting by local people, usually in or near their own homes; slags from large lead smelters are collected or bought by villagers, who burn it in order to recover the lead and sell it.

Likewise, health and safety can vary from complete protection from any contact with lead (see (b) above), to some protection, such as gloves and cloth face masks, to no protection whatsoever.

### 3.4.2 World Directory: secondary lead plants

**T**his article gives an overview of the number of lead recycling facilities world wide and the technologies used in these recycling facilities.

In: **World Directory: Secondary Lead Smelting**  
International Lead and Zinc Study Group (ILZSG)  
London, England

[1994]

#### Introduction

**T**his is the fifth edition of the Study Group's "World Directory: Secondary Lead Plants", following the original edition published in 1981 and the subsequent revisions in 1985, 1989 and 1991.

It has been prepared under the direction of the Sub-Committee on Production\* of the Study Group's Economic Committee and complements the listing of lead smelters and refineries operating solely or partly from concentrates and bullion contained in the "World Directory: Lead and Zinc Mines and Primary Metallurgical Works".

The Sub-Committee wishes to record its appreciation of the assistance received from Member Governments and from Government authorities and industry sources in non member countries in supplying information on plants currently in operation.

#### Smelters

**187 secondary** lead smelters are listed with a total annual capacity of 3.137 million. Of this, 42% is in North America, 28% in Western Europe and 14% in Asia, with smaller proportions in Eastern Europe (9%), Africa (2%) and South America (4%).

The largest plants are in the United States where the total capacity of nearly 1.1 million tons includes 3 plants of over 110,000 tons p.a. In Western Europe, medium sized plants (between 10-30,000 tons p.a.) are more general. In Asia (including Japan, Korea and Taiwan), South

America and Africa, small and medium sized plants predominate.

The most common type of smelter is the Rotary Reverberatory Furnace. It is operated in more than half (55%) of the plants, followed by the Blast Furnace (24%) and the Stationary Reverberatory Furnace (17%).

#### Refineries

**Total capacity** of 3.290 million tons at the 191 refineries listed is slightly higher than smelter capacity.

The largest proportion is again in North America (41 %), followed by Western Europe (30%), Asia (13%), Eastern Europe (8%), South America (5%), Africa (2%) and Oceania (1 %). Pyrometallurgical processing is almost universal.

#### Coverage

**T**he report covers secondary lead plants in all countries for which it has been possible to obtain information.

It should be noted that small plants with capacities for lead smelting or refining of less than 1,000 metric tons per year have been omitted from the report. As far as possible, plants remelting secondary lead materials which are not equipped with smelting or refining facilities have also been excluded.

#### Format

**C**ountries are listed alphabetically. Similarly, companies have been listed alphabetically under each country.

\* *Members : Australia, Belgium, Canada, Peru, Spain, United States of America*  
*Chairman: Mr. T. Keating (Australia)*





### Environmental implications

The battery constituents with the most potential for impacting the natural environment are lead and sulphuric acid. The impact of metals is accelerated by the presence of the acid because most of the metals attain their mobile ionic forms in an acid environment. Although metals are typically retarded within the top 25 cm of the soil under natural pH conditions, the mobility of the metals in the subsurface environment increases under acidic conditions, potentially resulting in groundwater contamination. Therefore, the primary environmental concerns with regard to management of used lead acid batteries relates to protection of soil and groundwater.

Once taken out of service, a battery is either:

- recycled
- stored on an indefinite basis
- transported
- inappropriately disposed of.

Each of these has environmental implications which are discussed below.

#### Recycling

The processing of used batteries, predominantly conducted at secondary lead smelters, has the potential for deleterious environmental impacts. This is particularly significant with regard to their slag management. At least two companies and Canada have recently been subject to considerable pressure related to their practices in this regard. It must be noted that secondary smelters are under strict regulations concerning all emissions, effluents and waste discharges.

The slag which is produced by the secondary smelters, is produced in their furnaces and is primarily composed of iron sulphide. The material is not considered toxic, however because of low levels of lead content ultimate disposal of the slag becomes a problem. One company in British Columbia has developed and is in the process of constructing a process which will derive saleable materials from the slag.

#### Storage

The term *storage*, as it is used here, refers to the retention of one or more batteries for a period of time until it is convenient to send them for recycling. This includes a broad range of potential situations, from the individual who has

placed one or two batteries in their garage or basement, to retailers who accept returns or act as a local repository, to household, hazardous waste drop off areas, to large-scale salvage operations which have stockpiled considerable numbers of batteries in anticipation of an increase in lead prices. (Some indirect evidence was collected during the course of this study to indicate that most provinces have at least one or two of the latter situations).

#### Transportation

Although transportation is a potential source of environmental impact, the direct impact upon the environment due to the transport of lead acid batteries is likely to be minimal. The most probable cause for such impact would be through accident as opposed to current management practices or technologies. The transportation of used lead acid-batteries is highly regulated. This is discussed in the following section.

In situations where large numbers of batteries are retained in one place for an indefinite period of time awaiting transportation, there is a need for best management practices in order to minimize the potential for damage to the environment. As batteries are added there becomes an increased probability that batteries in poor condition with casings which leak are being added. With time, there is increasing probability of degradation of these stored batteries because of exposure to the elements, accident or vandalism. This may result in potential release of contaminants into aquatic and terrestrial systems of the environment.

#### Inappropriate disposal

The inappropriate disposal of used batteries involves a range of disposal practices including dumping the used batteries in roadside ditches and poorly managed scrap-yards. Although these would not usually result in large accumulations of batteries, their location would be largely unidentified. It is at this point however, that the significance of the estimated ranges of the magnitude of inventory (i.e. unrecovered) lead-acid batteries in Canada becomes apparent. There is some evidence to suggest that major burial sites of used lead-acid batteries exist in

some pan of Canada. Once economic factors become acceptable, they may then be 'mined' [Wallace 1992]. This latter category is defined as inappropriate disposal because there is less

potential for complete recovery than the indefinite storage practice described previously. These sources have the potential for impacting air, soil and ground and surface waters.

## RECYCLING FACILITIES

### *(Battery Breakers and Secondary Smelters)*

- 1 Recycling facilities should be encouraged to recover all components of the used lead-acid batteries.
- 2 They should send the battery components which can not be recycled at the facility (e.g. acid from breakers) to an appropriate recycling facility rather than sending them for disposal.
- 3 The recycling facilities should adhere to applicable environmental regulations for processing, transportation and storage of used lead-acid batteries.
- 4 The recycling facilities must ensure that the residuals (e.g. air emissions, effluent discharges, etc.) from the recycling processes are managed in an environmentally acceptable manner and according to the applicable environmental regulations.
- 5 All recycling facilities should be registered with the provincial environment ministry. This could include licensing or approval requirements.
- 6 Recycling facilities should be encouraged to keep records, as part of a national data base, for determination of recycling rates on a national and regional basis.



### 3.4.3 Secondary lead smelting

**A**lthough this article is slightly outdated, it gives a good description of the technologies used in secondary lead smelters. Be aware of the fact that emerging technologies which use other techniques for smelting and refining are not discussed in this article. Some of these emerging technologies are addressed in the following article.

In: **Guidelines for the Control of Emissions from the Non-Ferrous Metallurgical Industries**  
United Nations Economic Commission for Europe

[1979]

#### Editorial comments

- (i) Refining temperatures range from 320-600°C.
- (ii) The melting point of lead is 327 °C.
- (iii) Nickel is not used as an alloying element, because it is known to cause short circuits in batteries.
- (iv) Aluminum is an alloying element used together with cadmium for low maintenance batteries only. It is not used in Europe. Elemental sulphur is added to remove copper, and oxygen is added to remove antimony and arsenic.
- (v) The SO<sub>2</sub> level of 5000ppm may not be acceptable in many countries: e.g. in France, it is 2000ppm

### GENERAL DESCRIPTIONS OF SECONDARY LEAD MANUFACTURING

**S**econdary lead manufacturing is defined as any metallurgical process that remelts or refines lead ingots, or lead-containing scrap or various types and produces metallic or lead compound which is further processed. To achieve this end, various furnaces are employed including blast, reverberatory and kettle-type furnaces. Processes which use some or all of these furnace types include storage battery production, lead compound manufacture, and metal fabricating.

The industry is generally composed of a number of small plants with a few larger plants,

although there is trend towards larger plants. Most plants are located close to their lead scrap sources and many are located in urban areas.

Production of lead in the Western world during the period 1970-75 averaged 3.85 million tons/year, of which more than one third was produced from secondary materials. Of this, secondary lead smelters accounted for about 60% although this percentage varied from a high of 76% for the US to a low of 44% for Europe<sup>[1]</sup>.

Statistics on the production and consumption of lead are contained in the primary lead chapter.

### PRODUCTION PROCESSES

#### General

**S**econdary lead is produced in blast (cupola) or reverberatory furnaces at temperatures of about 1250°C. Final refining is usually done in reverberatory or pot-type furnaces at temperatures of 700-900°C. The four main steps in processing secondary lead are sorting and preparing the alloy scrap according to size and alloy groups; smelting in blast or reverberatory furnaces; refining in pots or kettles and casting to ingots or final shapes. A principal product of the blast furnace is antimonial or 'hard' lead which can be cast directly into large blocks of varying weights.

Typical blocks weighing 1000kg are used as ballast and counter weights in the shipping industry. Final processing or purification of the metal involves the addition of chemical compounds to either reverberatory or pot type furnaces. These form drosses which usually float on the molten metal surface, and can be skimmed, through a furnace door, directly into skim buckets outside the furnace. Drosses contain impurities such as copper, nickel, and antimony. Further alloying can then be carried out if desired. Some scrap, such as cable sheathing, is pure enough to be added directly to a melting pot without further refining.

### Blast furnace (cupola) operation

A lead blast furnace is a vertical furnace with a circular cross section. The lower section of the furnace is water cooled while the upper section is lined with refractory material. A process flow diagram for a typical lead cupola, including pollution control equipment, is shown in **Figure 3.3**. Air is injected through pipes or tuyères near the bottom of the furnace and combustion of coke provides the heat necessary for melting and for the reduction reaction with the lead oxide. Raw materials are added through the charging door near the top of the cupola and molten lead is tapped off at the bottom. A typical raw material charge is composed of lead dross or other forms of lead oxide, coke, limestone, scrap iron and re-run slag. The cupola's function is to reduce oxidized metal. As the production cycle continues, the limestone and iron form a slag that helps prevent oxidation. The slag is tapped periodically while the flow of lead from the taphole at the base is continuous. The process is semi-continuous, the charge being added over a two-day period and the product withdrawn almost continuously.

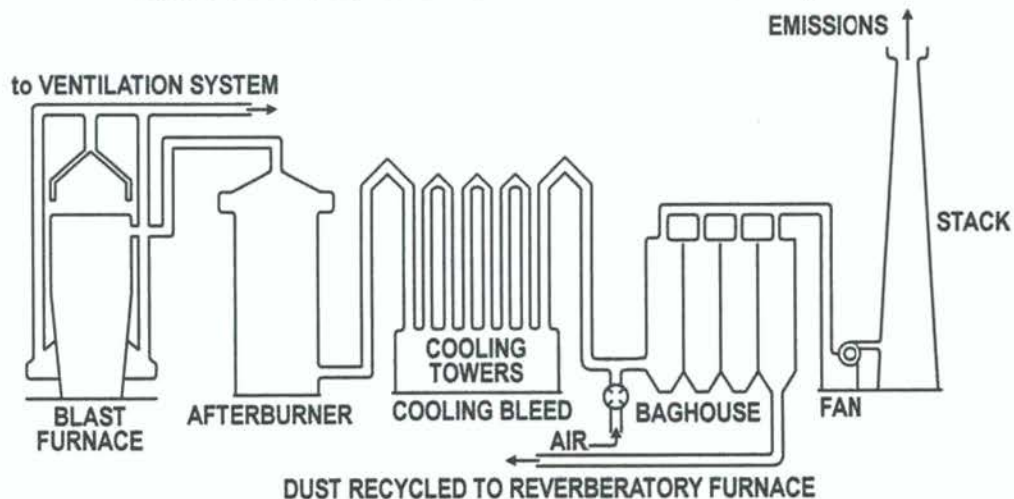
A molten metal level is maintained at the bottom of the cupola, above which a mixed mass of charge solids is contacted with air to burn the

fuel, reduce the lead oxide, and melt the product. Relatively high temperatures are reached in this section but the gases cool as they pass upward through the fresh charge at the top of the mass.

Coke is added with the charge or in alternate loads at the charging door. It is oxidized with blast air furnished by an air compressor to the tuyères at the bottom of the furnace. Gas flow is usually far in excess of blast-air flow because of infiltration of air at the charge door level.

The charge doors are usually designed to accommodate addition of charge materials by a bucket which is swung into the cupola and dumped. Other charging methods include conveyors or chute feeders. In the case of bucket feed, the charge doors must be large and are frequently left open or removed altogether. This allows a very high rate of air infiltration into the cupola. When air pollution equipment is installed, it is necessary to limit this infiltration to minimize the size requirement and operating cost. Torches or gas burners are often installed in the cupola, directly above the charging door, to burn carbon monoxide (CO). This after burner section must have some air seepage to provide for burning the CO, but is costly to operate without good sealing at the charge doors.

Figure 3.3 Process flow sketch of lead blast furnace or cupola



The composition of a typical lead cupola charge is shown in **Table 3.6**. This table also gives a rough measure of the feed rates for a 25 tonne/day cupola<sup>[4]</sup>.



Because the blast furnace is not efficient in retaining molten metal, it cannot be used for purification. The scrap, therefore, is usually charged in reverberatory or pot furnaces for melting and purification.

**Table 3.6** Typical composition of cupola charge (25 tonnes/day)

Component	Weight (% of total)	kg/hr average
<b>Dross</b>		
(15%) Metallic Dross	82.5	1100
Pb		
Sb		
Sn		
(85%) Oxide Dross		
PbO		
SbO		
SnO		
<b>Return slag</b>	4.5	60
<b>Scrap iron</b>	4.5	60
<b>Limestone</b>	3.0	40
<b>Coke</b>	5.5	75
<b>Total</b>	<b>100.0</b>	<b>1335</b>

### Reverberatory furnace operation

A reverberatory furnace is a long, rectangular, refractory-lined structure with an arched roof and a burner located at one end. Fuel is a fossil type – pulverized coal, oil or natural gas – and is burned separately from the metal being processed. A large part of the heat in the combustion gas radiates directly to the charge lying on the hearth below. At the same time a substantial amount radiates to the furnace roof and walls, and is reflected down to the charge – it ‘reverberates’ in the furnace. The hearth slopes slightly towards the rear of the furnace to allow for continuous tapping of the molten lead. A schematic diagram of a reverberatory furnace including air pollution devices is shown in **Figure 3.4**. Rotary (tube-type reverberatory furnaces) are used in smaller operations. Rotary furnaces are tapped periodically from ports which are sealed during rotation and firing.

Reverberatory furnaces are used in a number of ways in the processing of lead scrap to lead ingots. Some of these uses are: burnout, sweating, melting and purification.

The furnace charge may consist of automobile storage batteries; lead oxides or drosses and

skim; lead-sheathed cables; aircraft or ship ballast; or other miscellaneous, lead-bearing materials.

#### **Burnout**

The burnout operation is not strictly a smelting process but involves the incineration of materials which may be present in scrap metal such as plastics, rubber insulation, wood, paper and other combustibles. Burnout may also involve the decomposition of halogen-containing plastic materials such as polyvinyl chloride wire insulation which releases halogen acids when burned. These are toxic and may also produce objectionable odours.

#### **Sweating**

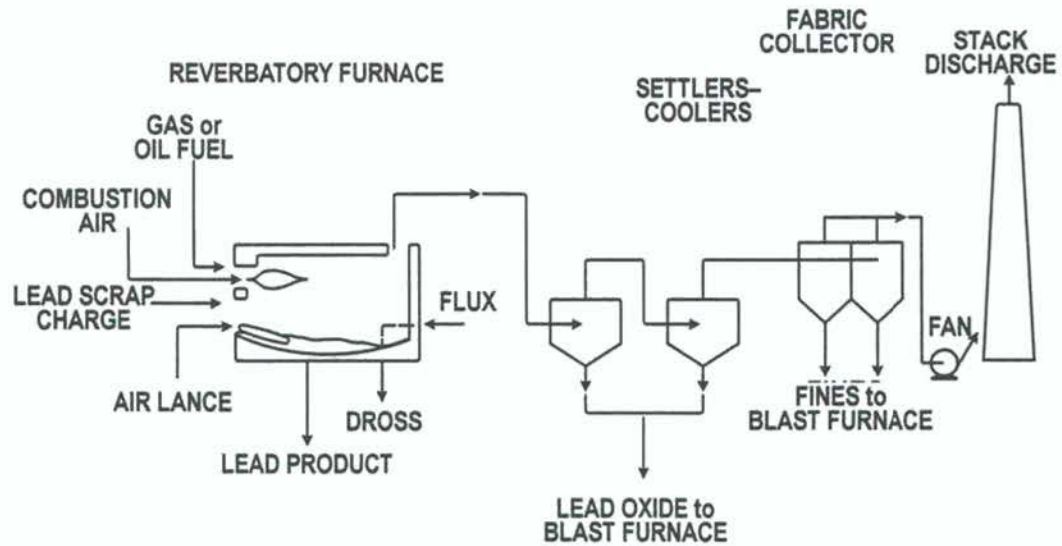
The reverberatory furnace is used for the separation of molten lead from various types of scrap containing both metallic and non metallic impurities. This is referred to by the industry as ‘sweating’ the melting of the low-melting-point constituent from the charge. This operation normally takes place at about 350°C.

A typical sweating heat involves charging scrap to the furnace hearth and gradually heating the scrap to a temperature slightly above the melting point of the metal to be separated. As the metal

melts from the scrap, it is tapped into ingots. Fresh charge is continuously added until all available scrap is depleted or the heat is terminated. The unmelted scrap must be periodically raked from the hearth for further disposal or sale.

Reverberatory furnaces may be used to melt lead pigs or ingots for casting. This process is more commonly carried out in indirectly heated furnaces such as electric or gas-fired crucibles.

Figure 3.4 Process flow sketch for lead reverberatory furnace



### Purification

The major use of reverberatory furnaces in secondary lead processing involves the purification of lead by removal of impurities such as iron, arsenic, antimony, and tin. The furnace may be charged continuously with molten metal from the cupola. In this case, air-blowing to oxidize metal impurities is either intermittent or continuous. The metal dross is removed by slagging and the molten lead is removed by tapping or casting into moulds on an intermittent basis.

Solid lead scrap may also be charged continuously to the reverberatory furnace. Material can be hand-fed through charging doors or fed continuously on conveyors. Here again, air-blowing and drossing can be either intermittent or continuous, with periodic casting.

Although the melting point of pure lead is 325°C, temperatures exceeding 1100°C are used for the purification of lead. These higher temperatures are required to bring about a reaction between the metallic impurities and the

oxygen charged into the metal bath. If lead oxide drosses are added to the charge, it is necessary to add a reducing agent such as granular carbon which reduces lead oxide to metallic lead.

It should be mentioned that reverberatory furnaces can be employed for the same purposes as a blast furnace and refining unit with reduction of lead oxides carried out prior to removal of impurities. It is, therefore, not uncommon to carry out the reduction, burn out, sweating and smelting operations sequentially in the same reverberatory furnace.

### Pot and kettle furnace operation

**P**ot and kettle furnaces are used for remelting, alloying, and refining. Remelting is usually done in small pot furnaces and the materials charged are most often alloys in ingot form. The pots used in the secondary lead industry range in capacity from 1-50 tons and most are gas fired.

Alloying normally begins with a metal lower in the percentage of alloying element desired. The percentage desired is calculated and the required



amount is then added. Common alloying elements include antimony, tin, arsenic, copper, and nickel.

The refining processes most commonly employed are for the removal of copper and antimony to produce soft lead, and the removal of arsenic, copper, and nickel to produce hard lead. For copper removal, the temperature of the molten lead is allowed to drop to 320°C and sulphur is added. The mixture is then agitated and copper sulphide dross is skimmed off. Aluminum added to molten lead reacts preferentially with copper, antimony, and nickel to form complex compounds, which can also be skimmed from the surface of the metal. The antimony content can be reduced to about 0.02% by bubbling air through the molten lead. Further reduction can be achieved by adding a mixture of sodium nitrate and sodium hydroxide and skimming the resulting dross from the metal. Another common refining procedure is known as 'dry drossing' and consists of introducing sawdust into an agitated mass of molten metal. The resulting reaction forms carbon which aids in separating the globules of lead suspended in the dross, and reduces some of the lead oxide to elemental lead.

#### Raw material

**R**aw materials for secondary lead smelters consist mainly of scrap batteries and lead bearing drosses. Other lead scrap includes electrical cable sheathing and miscellaneous lead alloys, of which the most important are babbitts. Some virgin lead metal is also used.

Captive secondary lead smelters recycle internally generated scrap or lead bearing

material. The most important of these are lead additive manufacturers and some battery manufacturers.

#### Emerging technology

##### **Bergsoe SB furnace process<sup>[7]</sup>**

**This process**, utilizing a shaft furnace, has been developed to smelt whole batteries thus avoiding the environmental problems associated with battery crushing, removal and disposal of non lead components and handling of the crushed material. The off gases pass through an oil-fired incinerator. Special precautions have to be taken to prevent a chloride build up in the recycled dust.

##### **Oliforno process<sup>[8]</sup>**

**This is also** a process for the treatment of whole batteries. The process involves incineration of the whole battery in a kiln, followed by a granulation of the metal/slag product. The off gases are passed to an afterburner, and indirect cooler before being cleaned in an electrostatic precipitator. The process produces more flue dust than the Bergsoe process and much of the sulphur in the feed passes into the off gases. The granular product is hygienic to handle and can be smelted at a high throughput rate in a short rotary furnace.

##### **Bergsoe flash agglomeration furnace<sup>[9]</sup>**

**This flash agglomeration furnace** directly melts the flue dust leaving the bag filter collection conveyors. This avoids the serious hygiene problem of handling lead flue dust.

It has general application to dust with a suitable melting point range, but is not applicable to dusts containing substantial quantities of zinc and tin oxides.

## EMISSIONS TO THE ATMOSPHERE

**D**ata on uncontrolled emission factors for the lead producing and refining processes are summarized in *Table 3.7*.

The factors in *Table 3.7* have been estimated by various techniques including source testing, process material balances and engineering appraisals by the Environmental Protection Agency (EPA) of the United States<sup>[5,6]</sup>.

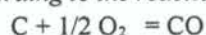
In addition to furnace operations, fugitive dust emissions can be a very important emission source if not properly controlled. Fugitive emissions occur from raw materials handling, sorting, crushing, outside storage, and furnace tapping and casting operations.

#### Blast furnace operation

**T**he chemical reactions taking place in a lead blast furnace are:



(a) Oxidation of coke for heat production according to the reaction



(b) Reaction of carbon with lead dross according to



The principal air contaminants of the process are carbon monoxide from partial oxidation of the coke, and particulate matter entrained by the highly agitated gases passing through the furnace. The particulate matter consists primarily of lead oxide, together with some iron oxide and oxides of alloy metals. There will also be some sulphur dioxide and carbonaceous material<sup>[4]</sup>.

In addition to the particulate matter entrained by gases flowing through the furnace, some vaporization of lead, antimony, and other metals will occur with these metals condensing as metal fume in the exhaust system.

### Reverberatory furnace operations

Emissions from a reverberatory furnace are similar to those from a blast furnace and consist primarily of particulate matter containing a considerable portion of lead oxide and oxides of alloying metals<sup>[4]</sup>. As in the blast furnace, lead, antimony, and other metals will vaporize and condense as metal fume in the exhaust system. Also, oxides of sulphur may be introduced as lead sulphate or sulphuric acid when lead batteries are remelted. In addition, significant quantities of hydrocarbons are emitted from the partial combustion which will release halogen acids. These are not only toxic but create objectionable odours when emitted to the atmosphere in significant quantities.

### Pot or kettle furnace operation

Emissions from melting kettles are relatively low when compared to those from blast or reverberatory furnaces<sup>[5]</sup>. Since the pot is used for many purposes, from melting pure scrap at just above the melting point of pure lead to refining the metal at higher temperatures, emissions vary in size and quantity.

Table 3.7 Uncontrolled emission factors for various lead producing and refining processes

Type of furnace or operation	Particulate kg/tonne	Lead kg/tonne	Sulphur oxides kg/tonne
Blast (cupola) furnace	120	28	45
Reverberatory furnace	113	27	42.5
Rotary reverberatory furnace	35	n/a	n/a
Pot furnace	0.4	n/a	n/a

## AIR POLLUTION CONTROL TECHNOLOGY

### General

Lead emissions can be minimized by the application of conventional control measures together with the use of sound engineering principles and good housekeeping practices. Control methods in the industry, to date, have been based on technology which can limit emissions to a high degree. This technology should be applied to all emission sources within a plant boundary including raw material storage as well as handling and conveying systems.

### Raw material handling and storage

Emissions to the atmosphere can be reduced by enclosing stock piles to eliminate dust entering the atmosphere. Practically, this involves keeping stockpiles inside a building equipped with a hooding system which captures dust from the piles and passes it through a collection device before exhausting to the atmosphere. This is applicable for any materials handling or processing operation which may cause particulate emissions such as crushing, sorting, and conveyor transfer. Conventional collection devices such as



cyclones, fabric filters, or scrubbers are the usual methods of control.

### Blast furnaces (cupola)

**E**missions from blast furnaces can be contained with conventional control equipment such as fabric filters or high energy scrubbers.

When fabric filters are used to control blast furnace emissions, they are normally preceded by a cooling tower and an afterburner as shown in *Figure 3.5*. The afterburner incinerates smoke and eliminates carbon monoxide. It should be designed to allow a residence time of approximately 0.5 seconds for the gases leaving the smelting section of the furnace. Excessive air leakage inward at the charging door will increase fuel requirements for the after burner section and should be eliminated or substantially reduced.

The fume loading leaving the afterburner section may be extremely high, as much as 10% of the material charged. A typical value quoted is 7% of the total charged. Gases leaving the cupola are normally cooled by infiltration of ambient air. Special care is needed in designing the system to prevent ignition of the filter bags in the event that the ventilating fan stops or the exit temperature becomes excessive, especially during 'burn down' at the end of a run.

With wet scrubbers, it is possible to limit the size of the scrubber by using water for quenching rather than infiltrated air. Quenching can be introduced immediately following the afterburner section of the cupola. The duct can be designed for a relatively low gas volume and should be made of corrosion-resistant material such as stainless steel or refractory-line carbon steel

EPA in the United States carried out emission tests on blast furnaces with results averaging between 0.002 and 0.017g/m<sup>3</sup> when the following control equipment was used:

- Afterburner and baghouse
- Afterburner, baghouse, and venturi scrubber
- Venturi scrubber

Production rate for the furnaces tested varied between 20 and 75 tons per day<sup>[2]</sup>.

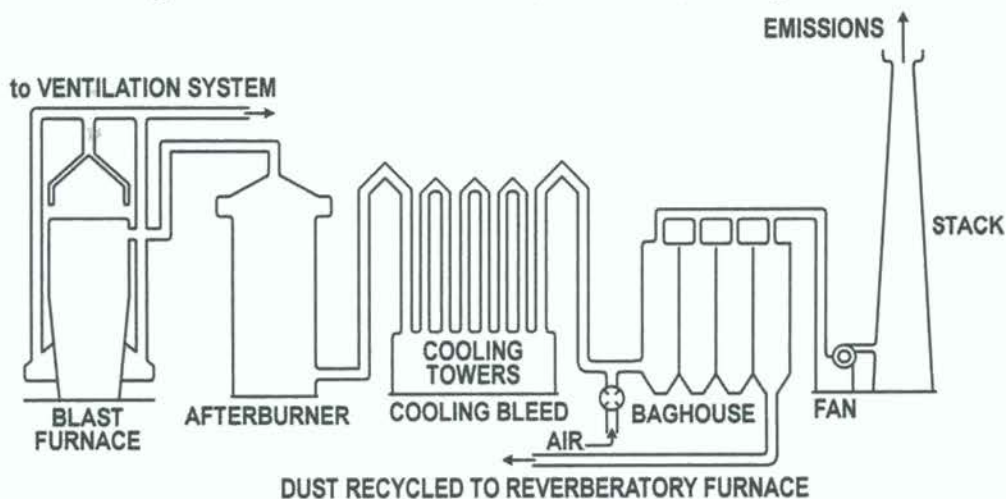
A blast furnace in Canada retrofitted with a baghouse, was tested in 1977. The emission test results were 0.040g/m<sup>3</sup> for particulate and 0.019g/m<sup>3</sup> for lead.

#### Note:

(A) For U. S. emission testing method, see reference 10.

(B) For Canadian emission testing method, see reference 11.

**Figure 3.5** Controlled blast furnace, afterburner, and baghouse



### Reverberatory furnaces

**E**missions from the reverberatory furnace (Figure 3.3) can also be controlled to a high degree (over 99%) by using conventional equipment such as fabric filters or high energy scrubbers. However, an afterburner may not be needed since there is usually sufficient air and temperature to incinerate carbon monoxide and hydrocarbons. Where afterburners are used, a luminous flame usually operates between 650°C and 800°C. The afterburner effluent gases are normally cooled to a temperature of 150°C or less. Evaporative cooling with a water spray and mixing with ambient air are practised, but a more successful method is the use of radiant convection U-tube heat exchangers. Care should be taken to prevent fabric filter temperature from dropping below the water or acid vapour dew point. Direct condensation of hydrochloric, sulphuric or hydrofluoric acids could then occur damaging or blocking the fabric filters. It may be necessary to have a baghouse both fully insulated and equipped with standby heating facilities to ensure minimum condensation, even during periods when the furnace is not being fired. Other precautions include coating the baghouse with epoxy-type materials to prevent corrosion. For uncontrolled temperature surges, a bypass damper may be required upstream of the baghouse.

Wet scrubbers can also be successfully used to control emissions from reverberatory furnaces. The most important advantage of a scrubber system is its ability to remove corrosive gases and mists as well as fine particulate matter from the furnace effluent gases.

In some cases, corrosive or noxious gases evolve from materials such as polyvinyl chloride (PVC) or Teflon in the scrap charged to the furnace. Hydrochloric acid and organic vapours will evolve from PVC-coated wire and hydrofluoric acid can evolve from material containing Teflon. To control these gaseous emissions, a packed absorption tower, in addition to a scrubber or baghouse, may be necessary.

Where battery plates are the principal source of scrap, concentrations of sulphur dioxide (SO<sub>2</sub>) between 2000 and 5000 ppm may occur. In this case, a wet scrubber may be required to remove SO<sub>2</sub> from the gas stream leaving a fabric filter.

The resulting acid waters would have to be neutralized prior to discharge into sewers or natural bodies of water. An alternative to acid water neutralization is the use of an alkaline scrubbing system. Caustic soda, soda ash, and other soluble saline materials can be used to remove sulphur oxides from the gas stream. A single wet scrubbing system could also be installed which would carry out both particulate collection and sulphur dioxide removal.

EPA test results from three controlled reverberatory furnaces averaged 0.004g/m<sup>3</sup>. These furnaces were production-rated at 20, 35 and 60 tons/day and all were equipped with fabric filters<sup>[2]</sup>.

### Pot or kettle furnaces

**H**igh efficiency (over 99.5 %) scrubbers and fabric filters are being utilized in well-controlled plants using pots for melting, refining or alloying purposes. Observations of nine smelters in the United States controlled by these devices have shown visible emissions of less than 10% opacity<sup>[2]</sup>. In some plants, the same collection devices used to control emissions from reverberatory furnaces and blast furnaces are used to collect emissions from pot furnaces. One pot furnace in Canada, equipped with fabric filters, was tested in 1977 and the results were 0.023g/m<sup>3</sup> for particulate and 0.007g/m<sup>3</sup> for lead.

Where arsenic is used as an alloying element, it is imperative that the melting kettle be completely hooded and that fumes be allowed to condense in a cooling unit prior to filtering in a high efficiency filtering device before the exhaust gas is emitted to the atmosphere.

### Other sources

**C**onventional control equipment including cyclones, high efficiency scrubbers and fabric filters are the usual means of controlling emissions from remelting, milling, handling, and burning operations for the various manufacturing processes. This would include the following:

- storage battery production
- lead compound manufacture including gasoline additives
- litharge and other compounds
- metal fabrication

### Fugitive emissions

**I**n addition to using control technology to contain dust and fumes from the various



emission-producing sources within a plant, good housekeeping is an essential method of preventing fugitive dust build-up. Canopy hoods over charging doors, launders, ladles and pouring stations are considered normal practice in well-controlled plants. Fugitive dust arises from a number of sources, the most important of which are materials handling and storage, slagging and tapping operations, handling of dust from dust collectors, and miscellaneous uncontrolled

sources. This problem is compounded by the dust settling out in the plant and becoming airborne again, either as a result of wind action or the movement of vehicles. The problem can be minimized by minimizing fugitive emission losses from the process, good housekeeping in the plant by paving areas and vacuuming the dust from paved areas and roadways and by washing adhering dust from vehicles, roofs, etc.

## EVALUATION OF CONTROL TECHNOLOGY

### General

The degree of particulate emission control for blast furnaces reverberatory and pot furnaces has been reported to vary between 98 and 99.5%, depending on when the control equipment was installed. Current technology, such as high energy scrubbers and fabric filters, achieves efficiencies of 99.5%. Secondary lead manufacturing industries can also utilize high efficiency equipment such as combinations of cyclones and baghouses or cyclones and high energy scrubbers.

Control efficiencies of 99.5% have been reported for battery plants. The goal for all

secondary lead producers and manufacturers should be the efficient containment of all emissions and fugitive dust sources with all captured dust disposed of in a non-polluting manner.

Carbon monoxide emissions can be easily controlled by the use of well-designed afterburners. The cost of these units can be significantly reduced by eliminating excessive air seepage through furnace charging doors.

Where sulphur dioxide removal is also required, best practicable technology would be high energy scrubbers utilizing alkaline solutions.

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### 3.4.4 Low waste technology for reprocessing battery scrap

This article is a case-study of a secondary lead smelter. Keep in mind that there are many different technologies and processes used in secondary lead smelting (refer to the directory of secondary lead smelters, and see the further background reading). This case-study gives a good overview of the wrecking, smelting and refining stages. The process is commonly used in many secondary lead smelters, although in practice you will often find modifications of this process.

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The Minerals, Metals and Minerals Society

[1989]

#### *A description of Blei- und Silberhütte Braubach – BSB Recycling GmbH*

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#### Abstract

Ways of processing battery scrap, advantages, disadvantages, constraints.

Targets of development of a new low waste technology:

- make use of most, if not all, constituents of old batteries and their conversion into highly valuable products,
- avoid non-useable fractions which have to be dumped,

- drastic reduction of pollution emissions and long term compliance to stringent pollution regulations considering acceptable operating and investment costs

- improvement of the working place conditions. Description of the battery breaking and separation system, of the desulphurization plant (where the sulphate in the paste is converted to sodium sulphate) and of the smelting/refining operations.

#### Introduction

Mining, smelting and refining of lead and silver at Braubach has an eventful history. First mining activities can be traced back to at least 1301 and first smelting operations to 1693. The actual "Blei- und Silberhütte Braubach" (BSB) was founded 90 years ago in 1899, and taken over by Metallgesellschaft AG in 1923.

In former times this smelter treated indigenous, and increasingly imported, concentrates to reach, shortly before World War II, a yearly production of about 60 000t of refined lead and 60 000kg of silver.

Primary smelting (i.e. starting from lead concentrates) was discontinued in 1963, but the refinery still treated foreign lead bullion and some raw material diverted from secondary sources (i.e. from scrap). Scrap was the exclusive raw material source at BSB from 1977/78 on.

1977 also marked the beginning of a co-operation with the Italian Tonolli group, which had a strong experience in secondary smelting. Tonolli took shares in BSB which is now owned on a 50% basis by Metallgesellschaft AG and IFIM International BV, Amsterdam another Tonolli participation.



## Generalities

**P**rocessing of battery scrap in secondary smelters mainly occurs:

- without any pre-treatment (tel quel) by smelting whole batteries in a blast furnace
- after decasing, respectively breaking either with or without separation of the battery components in a blast furnace (rarely) or in rotary furnaces (more frequently).

Processing of whole batteries or decased battery scrap has led in the past to several problems, which – independently from the selected smelting process – concentrated in the gas-cleaning sections of the plant:

- the casings (in former times usually hard rubber, nowadays predominantly polypropylene), burn, and the gases of decomposition have to be transformed into compounds trouble-free to the environment. This procedure (after burning) requires high additional quantities of energy and multiple quantities of conditioning air. Furthermore, polypropylene is a valuable material worth recycling (not burning!).
- about 50 % of the separators (between negative and positive electrodes) are made out of PVC. By thermal decomposition of PVC chlorine and metal chlorides evolve and concentrated in the

flue dust. As the latter has to be recycled, chlorine enriches and at a certain threshold a bleed-off for chlorine has to be found. The captation of some metal chlorides in bag filters may cause difficulties and additional environmental loads.

Other problems may occur:

- in relation with the sulphur content of the feedstock with slag and matte fall with SO<sub>2</sub> emissions
- in relation with the antimony content of the feedstock with an overloading of the refining section (if and when the production of soft lead is intended).

From those draw backs it appears that a foregoing separation of all constituents of scrapped batteries before melting resp. smelting is meaningful.

Other existing concepts of separation plants, however, overlooked some relevant aspects like:

- an increasing number of batteries (if not at all) are delivered with their acid content
- elimination of PVC
- recuperation of clean polypropylene, etc., – so that a new solution to an old problem had to be elaborated.

## New technological developments at BSB

**T**argets of the developments which occurred at BSB since 1977 were:

- to make used of most – if not all – constituents of old batteries and their conversion into highly valuable products,
- to avoid non-useable fractions which have to be dumped
- drastic reduction of polluting emissions and long-term compliance with stringent pollution regulations considering acceptable operating and investment costs,
- improvement of working place conditions.

With the processes actually in operation at BSB those objectives have already been fulfilled to a large extent:

- contrarily to current practice in other smelters the new plant of BSB is designed to treat

complete old batteries including their acid fillings. This diluted acid (10-20% H<sub>2</sub>SO<sub>4</sub>) can be used for metallurgical purposes or for pickling solution, avoiding the dissipation of tremendous quantities of acid (25-30% of the weight of the complete battery!),

- the careful breaking technology of complete old batteries (developed by Tonolli) is a prerequisite for the clear separation of the various constituents in definite fractions: metallic lead, lead paste, PVC and ebonite (hard rubber) respectively polypropylene. This, in turn, is a prerequisite for the re-utilisation of clean polypropylene granules.
- The battery paste is a mixture of lead oxide and lead sulphates. In conventional practice, the metallurgical treatment of this paste is linked to

a high slag fall and/or to high quantities of recycled products (lead losses!) as well as to high sulphur (SO<sub>2</sub>) emissions (1). To avoid those drawbacks a desulphurization process was developed in which lead sulphates are transformed in lead carbonate and anhydrous sodium sulphate. Lead carbonate can be treated (reduced) without any problem in conventional metallurgical furnaces (e.g. short rotary furnaces) and anhydrous sodium sulphate (99.5% purity, 10ppm Pb) is another valuable product.

- Ebonite (hard rubber), polypropylene (pp) and PVC are also separated from each other. Clean polypropylene scrap – 99.5% purity – is obtained as granules and ready for re-use. The hard rubber fraction, which is practically free from PVC (max. 1%), can be used as additional fuel, for example in cement kilns. Research is currently in progress to find an outlet for the PVC scrap.

In summary, the processing of complete old batteries now yields:

- metallic lead (from grids, pole bridges, etc.), which is molten to obtain lead bullion which has to be refined,
- lead carbonate (from desulphurization of lead paste) with less than 1% of residual sulphur, which is smelted to obtain a fairly clean lead bullion,
- anhydrous sodium sulphate (99.5%, 10 ppm Pb) for sale
- clean polypropylene granules (98.5% or 99.5% after further processing) for sale
- ebonite (hard rubber) with max. 1% PVC for sale
- PVC scrap and
- diluted sulphuric acid both for possible re-use – and the target of a nearly waste-free method of processing scrap batteries is reached at BSB.

Battery scrap is drawn from the stockyard by loaders and conveyed to a hopper (loader) which has side walls of stainless steel to resist the corrosion of the acid still present in the batteries.

From there, the scrap is carried to the crusher via a plate conveyor of stainless steel.

All the a.m. sections (stockyard, loader, conveyor belt and crusher) are drained to collect the acid which is conveyed to the acid tank for further use.

Crushing is carried out by a hammer mill to guarantee a careful breaking of the scrap.

The crushed material is discharged onto a wet screening drum where the separation of the paste from the remaining material occurs.

The latter is carried to the subsequent separation stage where polypropylene (pp), metallic lead (Pb), ebonite (hard rubber) and PVC are separated from each other.

PP is extracted from a separation tank and discharged into a bin, while Pb, hard rubber and PVC pass on to a further treatment into a hydrodynamic separator.

Lead grids and poles are extracted from the bottom of the hydrodynamic separator and conveyed to a bin for further treatment (melting).

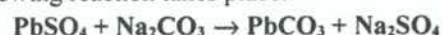
Ebonite and PVC are now separated from each other and conveyed to separate bins.

All process waters are collected in a circuit and recycled in the plant without any discharge into the water treatment plant.

The PP fraction is ground, washed, cycloned, heated and fed to a compounding unit.

The lead paste is conveyed to section b) (desulphurization plant).

Here the paste mud is charged to reaction tanks where, in the presence of sodium carbonate, the following reaction takes place:



The desulphurized paste is separated from the concentrated solution of sodium sulphate by means of a filter press.

After careful washing with water on the same filter the lead carbonate is discharged and stored for smelting.

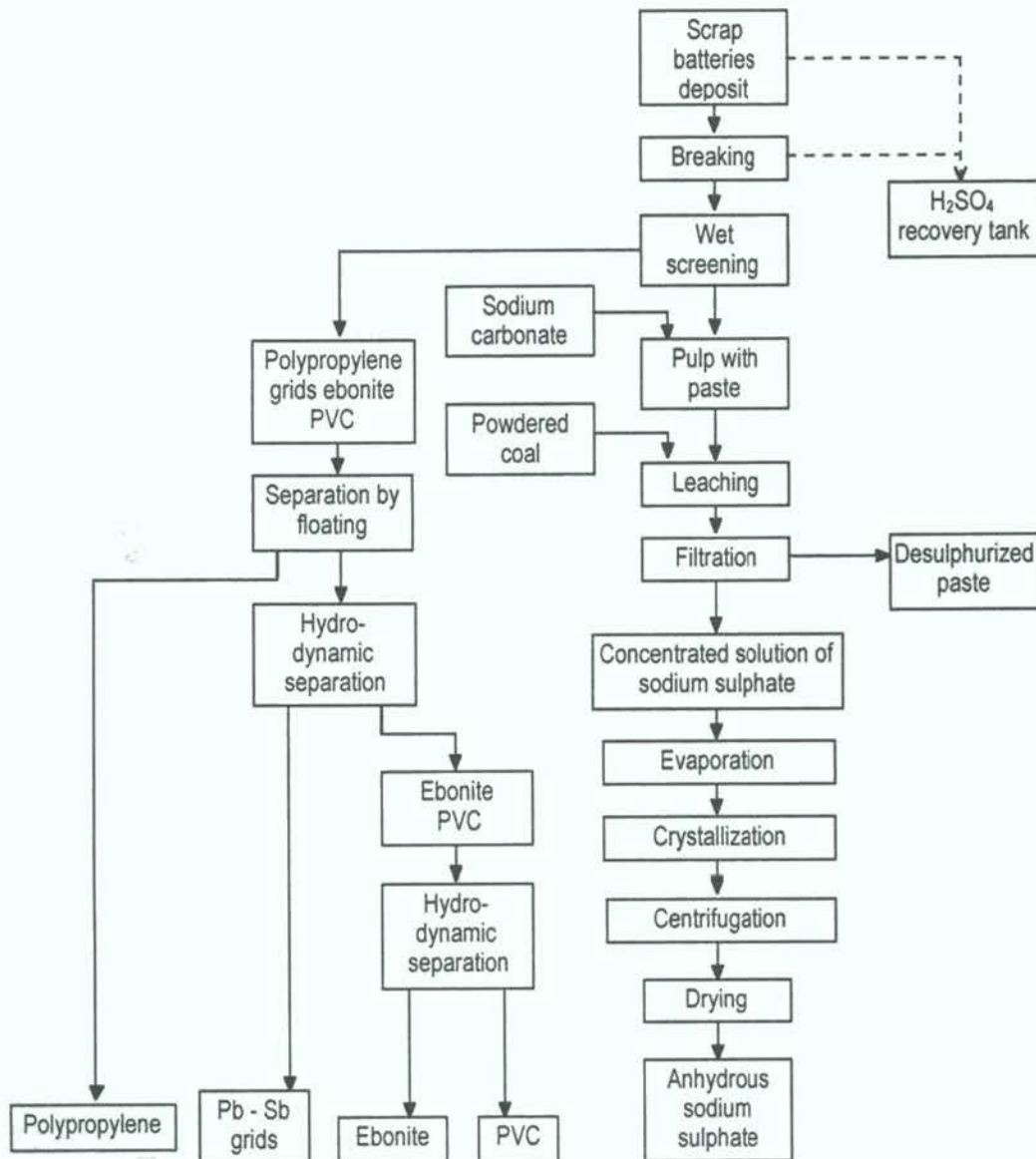
The clear sodium sulphate solution is pumped to an evaporation unit where the anhydrous salt progressively separates. After centrifugation sodium sulphate is dried in a current of hot air and stored in a bin ready for dispatching.

#### The process at BSB

The basic steps of the process flow-sheet now in use at BSB are depicted in *Figure 3.6*.



Figure 3.6 Processing of old batteries at BSB (simplified flowsheet)



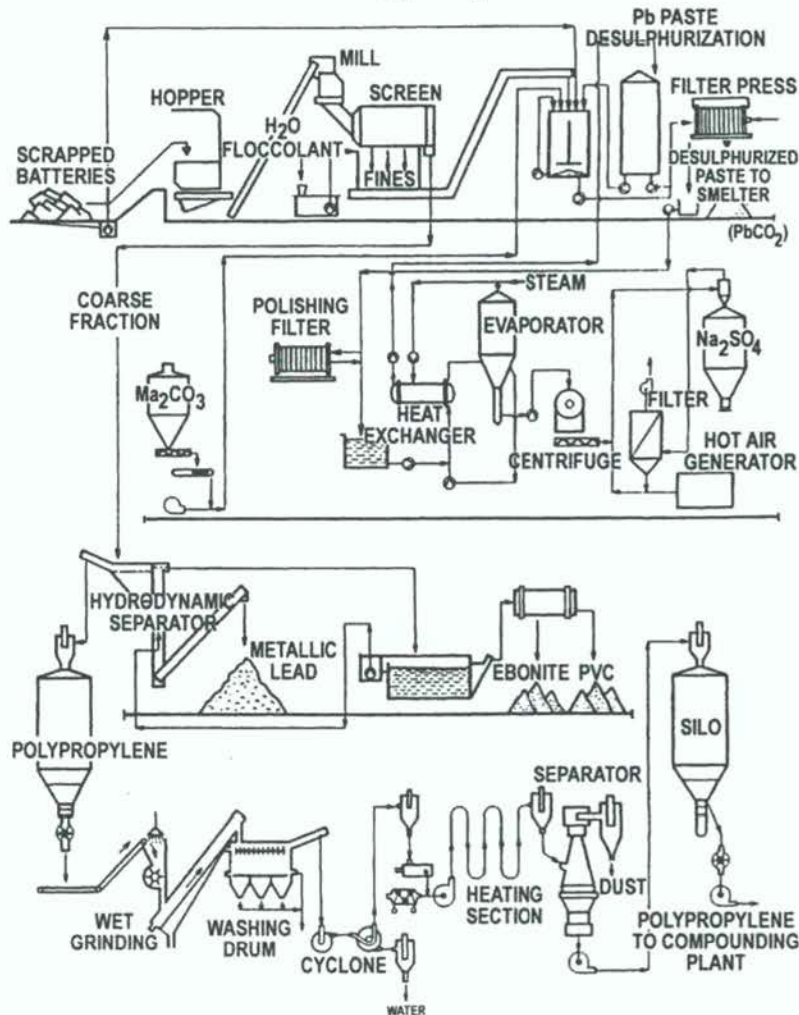
The plant can be divided in the following sections:

- a battery breaking and separation systems yielding metallic lead, lead paste, ebonite (hard rubber), polypropylene (pp), and PVC fractions,
- b desulphurization plant where the lead paste is transformed into lead carbonate also yielding anhydrous sodium sulphate,
- c polypropylene plant where PP fraction is upgraded to clean PP-chips

- d smelter where the metallic lead fraction is molten and the lead carbonate smelted to yield lead bullion which has to be further refined
- e refinery where the lead bullion obtained in the smelter is refined and, if required, alloyed to meet the various specifications of lead and lead alloy customers.

The equipment flowsheet of sections [a] and [c] is shown in *Figure 3.7*.

Figure 3.7 Equipment flowsheet of batter breaking and separation system and polypropylene upgrading at BSB



**M**etallic lead and lead carbonate are molten respectively in short rotary furnaces (Section [d] smelter equipped with four short rotary furnaces) to produce lead bullion and a discardable slag.

The principle of short rotary furnace operations including process gas cooling and dedusting is shown in *Figure 3.8*. The short rotary furnace is charged by the front door with the material to be molten or smelted. The reaction(s) take(s) place under the action of the heat supplied by an oil burner (in the prevalent case oxyfuel burners are preferred (2)). Metal and slag are tapped from the charging side while the dust-laden process gases leave the furnace through the rear end; they are

first cooled in a forced draft cooler, after quenching with the air drawn around the furnace (sanitary air) then dedusted in a bag filter before being discharged (as clean gases) into the atmosphere.

The last section ([e] refinery) is a classical but very simplified lead refinery. As lead bullion originating from secondary sources does not contain appreciable (and, consequently, valuable) amounts of copper, silver and bismuth, the steps of desilverizing, dezincing and debismuthizing (which are mandatory in primary lead refining!) can be by-passed and refining of secondary bullion is limited to:

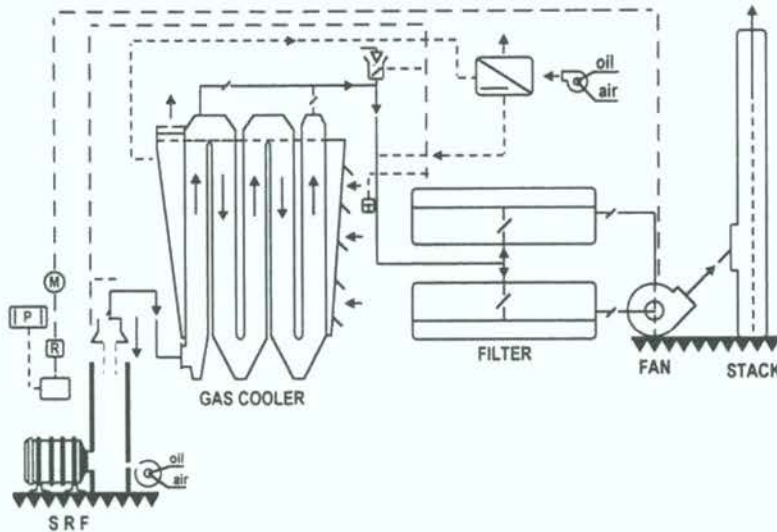
- drossing



- sulphur decoppering (to remove all but traces of copper, if any)
- softening (to remove tin antimony and/or arsenic, if required)
- alloying and final refining (if required, according to specifications).

The operations are carried out batchwise in kettles according to customers requirements. The metal is then cast in commercial shapes (45-50kg pigs or jumbos, as required), bundled (if required) and ready for dispatching.

**Figure 3.8** Short rotary furnace with gas cooler, filter and stack



### Summary

**B**y introducing several new technologies, BSB has achieved the goal to develop a nearly waste-free method for processing 60 000t/a of battery scrap.

Most of the constituents of old batteries are recovered and upgraded to high value products (refined soft and hard lead, PP granules, hard rubber, anhydrous sodium sulphate and diluted sulphuric acid).

Compared to classical methods:

- the amount of material to be dumped (e.g. slags) was reduced by 60%
- the amount of lead contained in slags was reduced by 80%
- SO<sub>2</sub> discharges to the atmosphere were reduced by 90%.

Moreover, the amount of fluxes required for smelting as well as the energy consumption were considerably lowered.

*Figure 3.9* shows a typical material balance for a Tonolli -battery breaking and separation system (CX) including smelting and refining of the products.

*Figure 3.10* shows in an impressive way how the lead emissions could be lowered by the introduction of various new techniques at BSB since 1977.

SO<sub>2</sub> emissions have also been drastically reduced since the introduction of paste desulphurization: see *Figure 3.11*.

The development of these new technologies was sponsored partly by the German Environmental Protection Agency (Umweltbundesamt), the Ministry of Research and Technology (Bundesministerium für Forschung und Technologie), local authorities (Land Rheinland-Pfalz) and the European Community. Their kind interest and financial support is gratefully acknowledged.

The Tonolli CX breaking and separation system was developed by Dr. R. Capetti and Dr. M. Olper.

**Figure 3.9** Typical material balance for a Tonolli CX battery breaking and separation system including smelting and refining

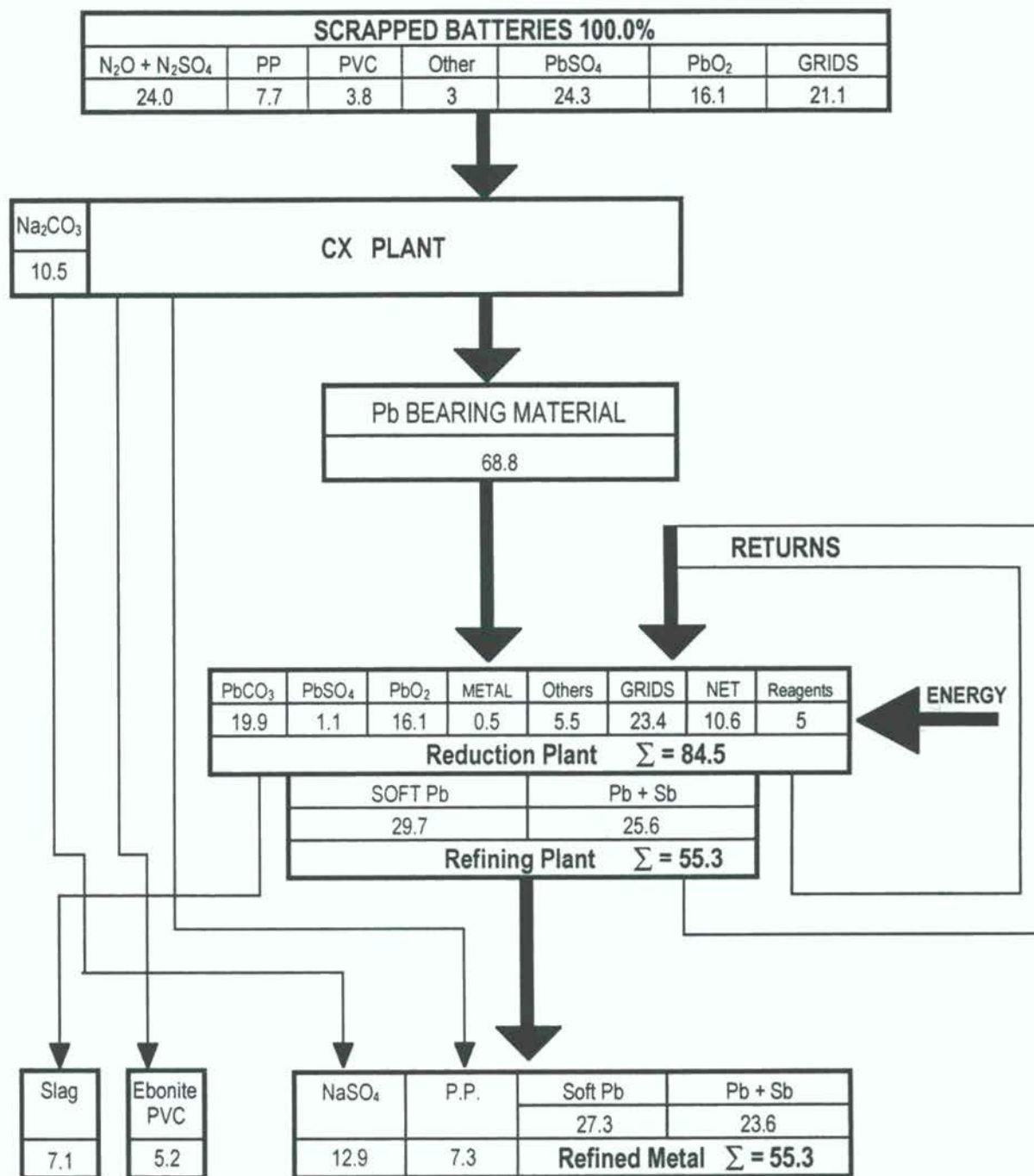
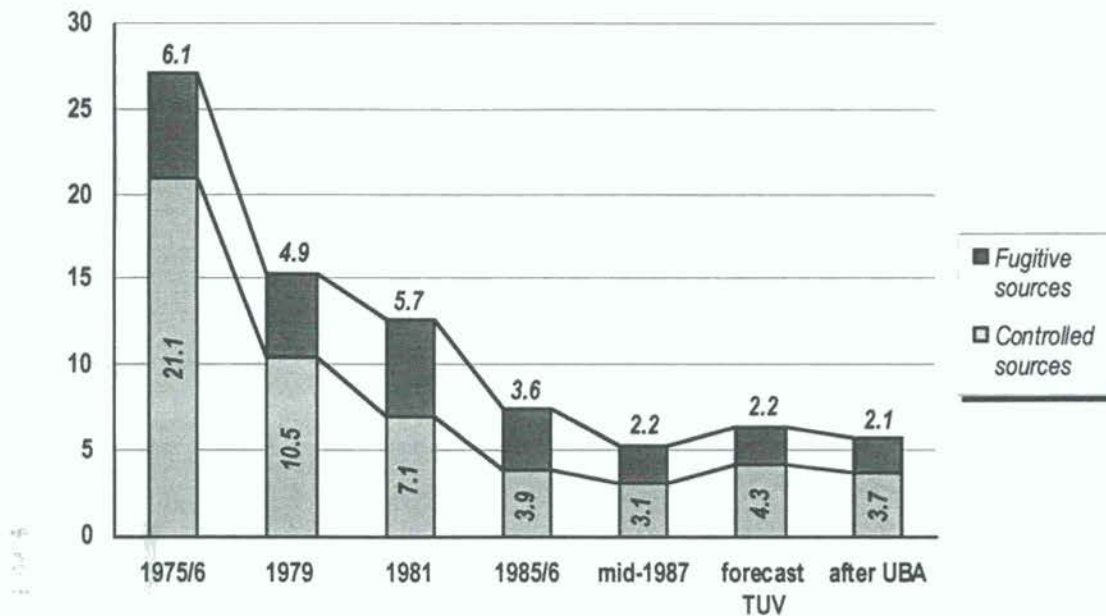
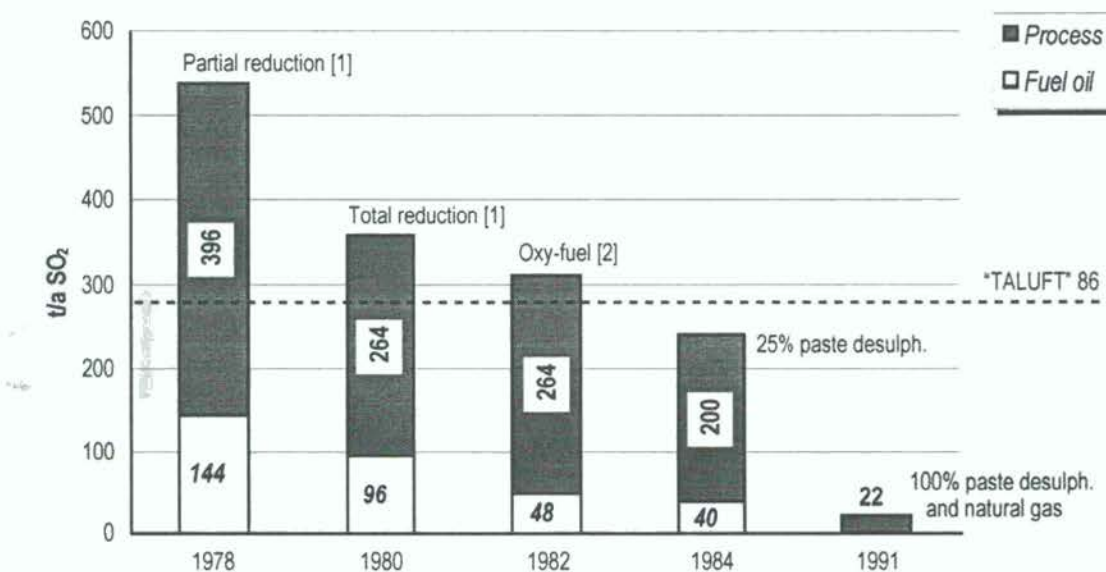




Figure 3.10 Emission register of BSB 1975/76 to 1987 (in t Pb/year)

Figure 3.11 SO<sub>2</sub> emission from the treatment of 60 000t/a of scrapped batteries at BSB

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### 3.4.5 Lead scrap processing in rotary furnaces

According to the world directory of secondary lead plants, the rotary furnace is the most currently used technique for smelting of secondary lead. Note, however, that this article does not cover all technologies which are being used for lead smelting. Refer to the references in *Part 4* of this training package for information on alternative smelting technologies and the forthcoming UNEP technical report.

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[1987]

## LEAD SCRAP PROCESSING IN ROTARY FURNACES: A REVIEW

MICHEL ROUSSEAU

### Introduction

High efficiency in lead scrap recycling has been well known for a long time<sup>[1]</sup>. Lead recycling ranged – in relation of the 1984 consumption – at 46 % in the F.R.G., 53 % in the USA and 49 % in the Western World. Most of the lead scrap is recovered from batteries.

Formerly, the lead scrap had been processed mainly in reverberatory and shaft furnaces or even in rotary furnaces (RF). The direct smelting of battery scrap entrains an expensive pollution control and high operating costs because of slag

recirculation, coke consumption, losses in slag and matte. Nowadays, mechanized battery wrecking plants allow selective separation of casings and separators from metallic Pb (grids, poles, solders) as well as lead in non-metallic form (PbSO<sub>4</sub>, PbO, PbO<sub>2</sub>, contaminated with some Sb) frequently called paste. Because of their high performance and flexibility in metallurgical processing (melting, reducing, oxidizing and selective pouring) the RF supersedes the reverberatory furnace world wide.

### Characteristics of rotary furnaces

Different characteristics of RF are described in *Table 3.8* and shown in *Figure 3.12*. Even complex secondaries may be treated in RF<sup>[2]</sup>.

The shell rotation (usually up to about 1.5 rev/min) allows high mixing efficiency and a high utilization of the heat. The SRF, developed according Prof. Dr. Kohlmeyer, is close to the ideal spherical shape (minimum outside surface for a maximum working capacity). A Lance-type burner usually is installed at the rear end of the furnace and, thus, the thermal performance of the SRF has been increased. The SRF is charged by

the front door. In modern plants fork-lift with a rotating spoon are used for charging.

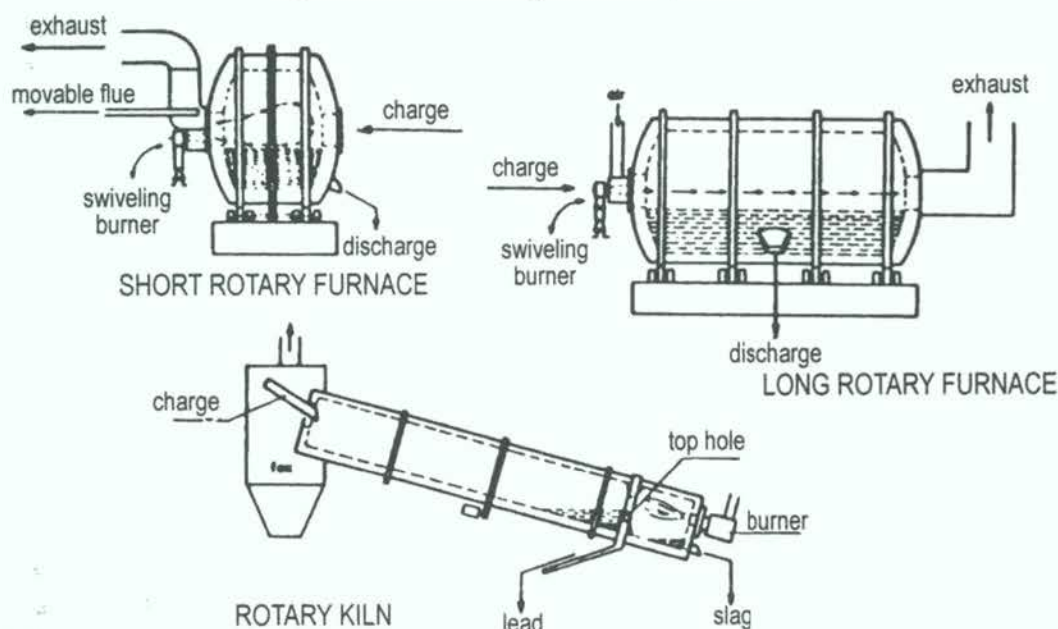
The LRF fired at the front end by a burner must be switched-off and moved before charging the furnace. The ratio of the surface of the bath to the quantity of the charge may be advantageous for particular metallurgical steps, e.g. oxidation or selective fuming.

The TRF operates continuously and countercurrently. It is mostly unlined (contrarily to SRF, LRF or RK) and is fired directly or better indirectly. The unlined TRF is generally used as a sweating furnace (SF)<sup>[2]</sup>. The RK is lined and operates continuously and countercurrently.



Table 3.8 Characteristics of rotary furnaces

Furnace type	Ratio length to diameter	Usual dimensions in m	Pb scrap processing	
			capacity	average throughput
Short rotary furnace (SRF)	1.0 - 1.5	$\varnothing = 2 - 4$ $L = 2 - 5$	7 to 20 t (per batch)	5,000 to 20,000 tpy
Long rotary furnace (LRF)	1.5 - 3.0	$\varnothing = 1 - 4$ $L = 2 - 6$	0.5 to 10 t (per batch)	500 to 15,000 tpy
Tubular rotary furnace (TRF)	3.0 - 11.0	$\varnothing = 0.5 - 1.5$ $L = 3 - 6$	not significant	15,000 to 35,000 tpy
Rotary kiln (RK)	11.0 - 25.0	$\varnothing = 2.4 - 4.5$ $L = 40 - 75$	8 - 20 % of vol. or 0.1 to 2.0 t per m <sup>3</sup> .d	up to 70,000 tpy

Figure 3.12 Different types of rotary furnaces<sup>[1]</sup>

### Operations features

The fractions obtained from the wrecking of old batteries are generally processed separately. The metallic fraction is remelted without any difficulty and reused for alloy production. The RF throughput (depending on the separation of grids from paste) may come to 100-150tpd or more, the average fuel consumption is about 70-80kg oil/t of lead. The oxides resp. slag are generally left in the RF. They build up after numerous charges and are, finally, reduced by

fluxes and reductants. By controlled oxidation it is possible to lower the Sb-content of the bullion, eventually up to bullion quality (e.g. 0.2-1.0% Sb) which could be refined to soft lead. In this case the slag (enriched in Sn, As, Sb) has to be reduced to a hard lead.

The processing of oxidized/sulfatized fractions is slightly complicated. Additions of reducing agents (e.g. coke breeze, petroleum coke) and fluxes are required. Generally, a Na<sub>2</sub>O-, CaO-,

ently SiO<sub>2</sub>-bearing slag is preferred because of its low melting point. Its lead solubility is low and, to a certain extent, Cl (ref. residual plastic) S, As can be collected. Iron chips and turnings can be added for S-binding (precipitation). Only discontinuous processing of paste (in SRF, LRF) may result in the production of different bullions. Nowadays, however, this is not advantageous since Sb-poor pastes are being produced increasingly in modern battery wrecking plants. Paste is therefore mostly processed by smelting/reducing – often combined with precipitation – in a single step (slag tapped after each batch) or in multiple steps (slag built up in RF and reduced later on in situ). The latter leads to a decreasing bullion throughput after each charge, which is normally not compensated by faster melting. The RF throughput of oxidized/sulfatized fractions is normally 35-55tpd. The average fuel consumption amounts to about 80 to 100kg/t of bullion (against about 75 to 120kg/t in the RK)<sup>[3]</sup>.

Alternatively, the desulfurizing of paste by means of NaCO<sub>3</sub> – as recently practised in industrial plants – improves the environmental conditions. The PbCO<sub>3</sub> (almost free of Cl and S) is simply reduced at 800-900°C.

Usually the RF are lined. Firstly, the thermal efficiency of RF and, secondly, the selection of

refractories are some of the keys to success. At an upper working temperature (900-1100°C) the Pb-oxides are very corrosive because of the eutectic PbO-SiO<sub>2</sub> at 715-730°C, resp. PbO-Al<sub>2</sub>O<sub>3</sub> at 865°C. Chromium- and/or magnesite-bearing refractories are resistant under these conditions. Magnesite resists to Pb-corrosion and to the action of alkali fluxes but is corroded by acid slag, forms accretions with Fe-rich slag and is less resistant to frequent changes of temperature. Additions of Al<sub>2</sub>O<sub>3</sub> resp. Cr<sub>2</sub>O<sub>3</sub> improve magnesite properties. Chromium-magnesite has a greater resistance against acid and basic slags as well as against alkali fluxes, and (under 1500°C) against iron oxide. Their chemical corrosion occurs because of lead chromates with low melting points (841°C to 928°C). A combination of the a.m. properties is required. Normally chromium is used (e.g. 60-75% MgO, 12-16% Cr<sub>2</sub>O<sub>3</sub>) or improved magnesite (e.g. 77-82% MgO, 6% Cr<sub>2</sub>O<sub>3</sub>). The life of the latter quality may last 3 to 24 months. If the classical burner is replaced by an oxy fuel burner, the lining concept may become obsolete as the differences in temperatures between bath and lining must be maintained in a certain range.

### Case history

**T**he Blei- und Silberhütte Braubach GmbH, Braubach, FRG, processes scrap ex battery wrecking plant, in four ø 3m x 4m SRF of abt. 40 000tpy total capacity. The SRF are fired by 360kg/h and lined with magnesite-chromium bricks<sup>[4]</sup>. As a first example the discontinued processing of fractions from Stolberg (see later on) will be described. The metallic fraction is directly melted. The Sb-content had been decreasing since the grid alloys contained less Sb: from 6 to 8% Sb round 1970, to 3.9% Sb round 1980 (up to abt. 2.6% Sb at present). Non-metallic fractions are processed to bullion by means of soda, CaO, SiO<sub>2</sub> and Fe chips. The reduction/precipitation method allows a direct lead recovery of more than 80% and a limitation of dust generation. *Figure 3.13*<sup>[3]</sup> shows the material balance by processing of middlings

(75% Pb thereof 14.5% Pb met., 1.5% Sb, grainsize 0 - 0.5 mm), and of slurry (65% Pb thereof 3 % Pb met., grainsize 0.5-5.0 mm).<sup>[4,5]</sup> The resulting bullion contains abt. 1.2 to 1.7% Sb.

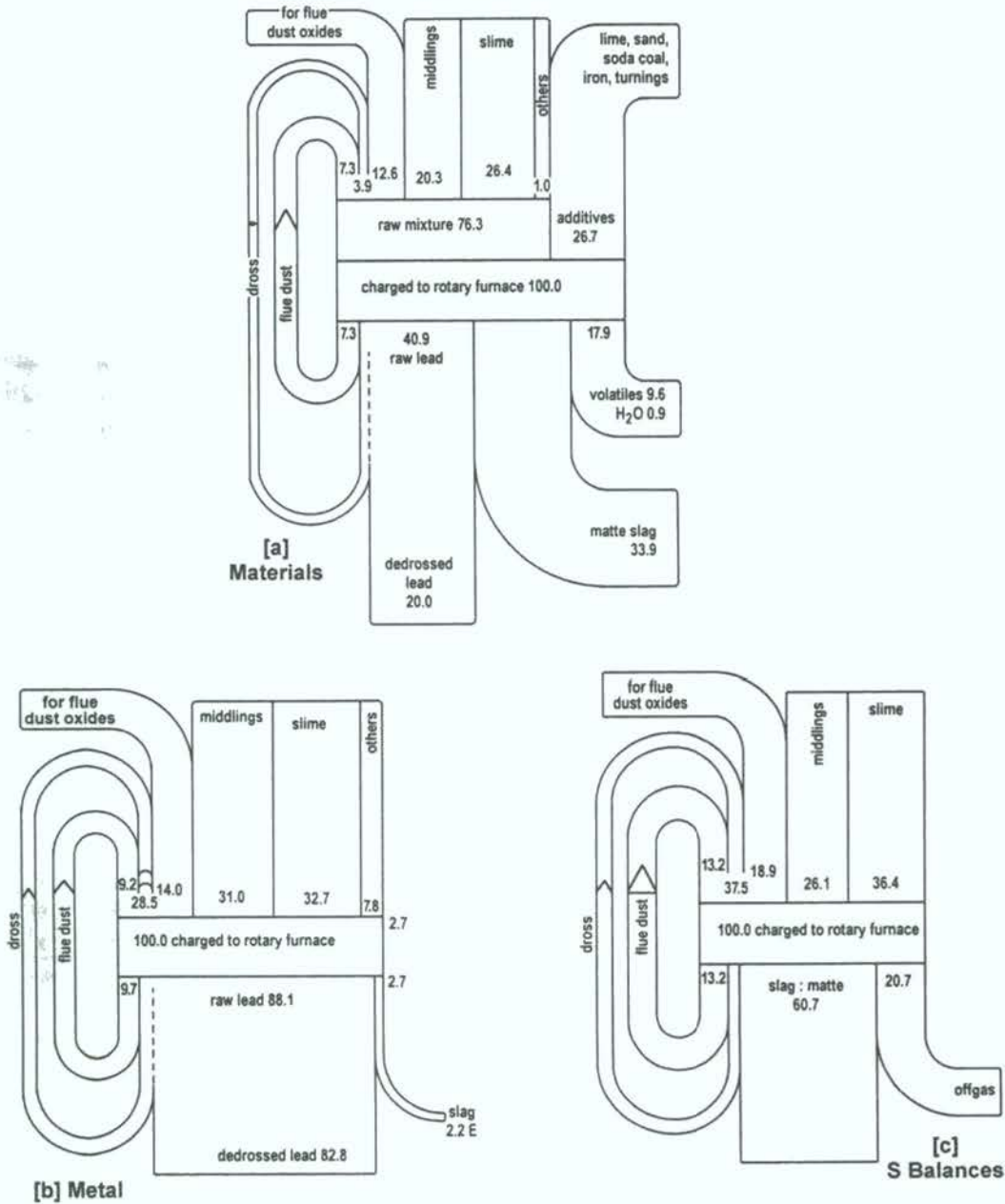
Nowadays, a new battery wrecking unit (25 t/h) produces only two fractions with higher purity and better selectivity with regard to casings and separators: grids (with abt. 94-96% Pb + Sb) resp. paste (with 73-75% Pb + Sb) accounting for abt. 27-28% resp. 48% of the weight of old batteries. The actual overall consumption figures per t grid plus paste amounts to abt. 6 to 9kg refractories, 80-90kg oil and 100-120kWh, resp. 40kg oil and 50kWh, when using an oxy-fuel burner (which generates 2.2m<sup>3</sup>/t oil). When using an oxy-fuel burner the generation of flue dusts decreases from 193kg/h to 57kg/h. In addition the



productivity increases slightly from 5.3 charges per day and furnace to 5.7 and the losses in slag decrease by 0.7 unit Pb<sup>[6]</sup>. Presently, the paste is

desulfurized with Na<sub>2</sub>CO<sub>3</sub>. The resulting PbCO<sub>3</sub> is reduced in SRF.

Figure 3.13 Processing of non-metallics in SRF<sup>[4]</sup>



Since 1974, Penarroya processes the scrap ex battery wrecking plant (capacity 20t/h) in SRF at Villefranche/Saone, France.

There are two  $\varnothing$  3.6 x 5m furnaces with a total capacity of abt. 30 000tpy, mostly used for reduction operations (at 950°C). Flue dusts, fines, Pb-bearing mud, drosses are being pre-mixed with additives (Fe-chips, Na<sub>2</sub>CO<sub>3</sub>, anthracite) and pelletized. This cuts down flue dust generation to 3.4% bullion. The average throughput per furnace amounts to abt. 92kg oil, 45kWh for mere reduction and 105kWh for the gas cleaning system. The latter figure illustrates the importance of environmental protection in investment and production costs. The overall recovery (reduction and melting) of Pb amounts to 97.7% and of Sb to 98.9%<sup>[7]</sup>.

In 1979, Berzelius GmbH Stolberg, FRG, commissioned a modern plant with two LRF  $\varnothing$  3.6m x 5.3 / 6.0 m, fired by 200kg/h burners and lined with magnesite-chromium. They processed mainly by-products of the primary lead smelter, but, in the past, fractions of the battery wrecking plant<sup>[1]</sup>. The furnaces are covered by hoods. The aspirated hygienic air is combined with the process off-gases (originating from a waste-heat

boiler) before being fed to a Jet bag filter (40 000Nm<sup>3</sup> /h for each furnace<sup>[8]</sup>).

A TRF used as SF for melting of heavy media sink (mostly made of grids) worked by NL Industries at Pedricktown, NJ, USA.

The SF  $\varnothing$  1.2 m x 6.1m worked countercurrently, fired from the discharge side by one burner. Excessive plastic contents of the feed lead to burner shut-down and may require the use of the burner fan as air blower. 85% of the feed reported as Pb and 15% as dross<sup>[3]</sup>.

At Pedricktown drosses and complex Pb-bearing materials were fed to a R.K. according to technology developed by Preussag AG Metall at Oker, FRG, [103]. The R.K.  $\varnothing$  3.1 / 2.4m x 54m rotating at 0.3-1.1 rev/min, was fired by a 37GJ/h burner. The lining of the kiln (392t) consisted mainly of alumina bricks for feed and preheating zones, resp. magnesite chromium for the reaction zone. Petroleum coke, cast-iron chips and soda ash were added. The slag (containing 20% unburned coke) flowed continuously out of the kiln. The Pb remained in the kiln and was tapped by intermittently stopping the kiln. Control of slag viscosity (additives) and temperature (burner control) are the keys for high metal recoveries. R.K. performances are shown in *Table 3.9*.

**Table 3.9** Performances of a rotary kiln <sup>[3]</sup>

Charges	Throughput (tpd)		Bullion
Pellets/middlings	200	225	> 1.25% Sb
Plant scrap	225	288	6% Sb
Grid metal/pellets	180	200	3% Sb

## Conclusion

The dismantled old batteries and, increasingly, fractions out of battery wrecking plants are processed in rotary furnaces worldwide. The rotary kiln process is employed in some cases only, since the investment is high and the thermal efficiency is lower than of other rotary furnace types.

The tubular rotary furnace is well-known in the non-ferrous recycling industry for complex secondaries but rarely employed for Pb recycling.

Highly metallized scrap can be continuously processed in this TRF. It could be connected downstream to a battery wrecking plant.

The long rotary furnace is not so frequently used as the short rotary furnace. Both are suitable for melting, reducing/oxidation steps and allow selective tapping. but the SF normally has a higher thermal efficiency and a better ratio of working capital to furnace volume as well as of investment productivity.



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### 3.4.6 Lead smelting: occupational safety and health guidelines

**T**his article gives an example of safety and health guidelines for (secondary) lead smelting. The article also gives you an idea of what preventative measures can be taken to avoid exposure to lead. When addressing human exposure at the workfloor, it is important to realize that emissions from the secondary lead smelter can vary considerably depending upon the degree of *good housekeeping practice, supervision, and control exercised at the plant.*

In: **Occupational Health and Safety Guidelines**  
 The World Bank, Office of Environmental Affairs  
 Washington DC, USA

[1984]

#### Editorial comments

- (i) Note that personal protective equipment is *always* necessary when working in a lead recycling facility, even if all appropriate emission control measures are installed.
- (ii) The guidelines given in this article were produced by the World Bank in 1984. Many national agencies produce their own guidelines, and users are encouraged to update this information regularly. Currently, guidelines for the European Community are being developed.

The World Bank  
 Office Of Environmental Affairs

April 1984

## LEAD SMELTING

### Occupational Safety and Health Guidelines

#### Introduction

1 In the lead smelting industry, serious safety hazards are burns from splattering and streaming of molten metal or slag, injuries from machinery, and strains from lifting and pulling. Other types of injuries are to the eyes, slips and falls and from moving objects.

2 The most serious health hazard is from dust and fumes. However, exposures coming from lead or other chemicals such as arsenic, sulphur dioxide, carbon monoxide, from excessive noise and from heat stress can also be dangerous.

These guidelines will cover recommendations on safety and health that will help prevent and reduce accidents and occupational diseases among employees.

#### Safety

3 Good housekeeping practices should be developed to reduce accidents. Individuals should be assigned clean-up responsibilities. Maintaining a clean and orderly workplace will reduce the danger of fires. Combustible materials will be stored in places which are isolated by fire resistant construction.

4 Well constructed bins for the storage of large quantities of raw materials will reduce the chances of injuries due to the falling of heavy materials.

5 Mechanical handling equipment must be provided for heavy loads.

6 All machinery must have guards on all moving parts to protect workers from injury.

7 Electrical equipment must be grounded and checked for defective insulation. All electrical installation and equipment must be in accordance with the standards of the National Electrical Code.

8 When necessary, the workers will be provided with personal protective equipment, including adequate clothing, safety helmets, non-slip footwear, face protection, gloves, aprons, leggings, etc.



## Health

### Lead

9 Lead is the major toxic product in the air in lead smelting and refining operations. Poisoning may occur through the inhalation of fumes and dust or accidental ingestion of dust. Other metals, such as arsenic, antimony, copper, silver, zinc, gold and bismuth are found in the ore and generate fumes or dust which may be hazardous.

10 Lead poisoning symptoms include loss of appetite, metallic taste, anaemia, headache,

nervous irritability, muscle and joint pains, and abdominal cramps. In the advanced stages of chronic poisoning, several body functions and organs, such as the liver, kidney and nervous system may be affected.

It is necessary to monitor the plant for lead and other metal fumes and dusts, and exposure should not be allowed to go above the following threshold limit values (TLVs):

Lead	50 $\mu\text{g}/\text{m}^3$
Arsenic and compounds (As As)	10 $\mu\text{g}/\text{m}^3$
Antimony and compounds (As Sb)	0.5 $\text{mg}/\text{m}^3$
Copper fumes	0.2 $\text{mg}/\text{m}^3$
Copper, dusts and mists	1 $\text{mg}/\text{m}^3$
Silver, metal	0.1 $\text{mg}/\text{m}^3$
Zinc oxide fumes	5 $\text{mg}/\text{m}^3$

### Editors Note:

Readers are encouraged to consult relevant authorities for recent updates of national TLVs. Refer also to the IPCS Materials Safety Data Sheets in Part V.

12 Local exhaust ventilation should be provided for all processes which generate lead fumes or dust. Good housekeeping and personal hygiene practices can reduce the amount of lead inhaled and ingested. Dust control measures, preferably hosing down with water, should be undertaken in all dusty areas to help reduce it. Separate lockers for work and street clothes should be provided. It is forbidden to eat, drink and smoke on the job. If circumstances dictate, the use of approved respirators is recommended. A co-operative program involving management, the industrial hygienist and the plant physician is strongly recommended. In order to control excessive absorption of lead and eliminate lead poisoning, this program should include the following points:

- a Air levels breathed by the employees must be monitored.
- b Periodic medical examinations for all employees, including the level of coproporphyrin or aminolevulinic acid (ALA) in the urine. The use of protoporphyrin free of erythrocyte or zinc protoporphyrin in red blood cells, is another process to screen, however it does not correlate as well at poisoning levels. If one of the tests is positive, it will be confirmed

through analysis of the level of lead in the blood, which will not exceed 75 mg of 100 grams.

- c Regular analysis of the air and biological concentrations will dictate the measures to take for reducing the hazards. An excessive amount of lead levels will require decreasing fumes and dusts by technical measures; the use of approved respirators and, if necessary, removal of the worker from the work area.

### Other air contaminants

13 Sulphur dioxide may occur from the furnaces during the roasting of ores. This contaminant irritates the mucous membranes of the upper respiratory tract. Chronic effects include rhinitis, dryness of the throat and cough.

14 Carbon monoxide is a colorless and odorless gas which results from incomplete combustion. Symptoms of poisoning are headache, fatigue, poor judgement, shortness of breath, weakness and dizziness, leading to nausea, vomiting and at high concentrations unconsciousness.

15 It is necessary to monitor those air contaminants, whose levels should be kept below the following TLVs:

Carbon monoxide	50 ppm	55 $\mu\text{g}/\text{m}^3$
Sulphur dioxide	5 ppm	10 $\mu\text{g}/\text{m}^3$

Refer to *Editors Note* on previous table.

16 If workers are exposed to excessive amounts of toxic products, engineering measures will be taken. The best solution to capture and remove these products is to use local exhaust ventilation.

17 Roasting and smelting operations produce other irritating gases such as hydrogen sulphide and nitrogen dioxide. These irritating fumes may cause or intensify disease in humans, harm plants, damage paint, concrete and metals.

#### **Heat stress**

18 Workers can be exposed to excessive heat, particularly at the furnace and refining operations. Early symptoms of heat stress are weakness, extreme fatigue, dizziness, nausea, headache and thirst. More serious symptoms are leg, arm and stomach muscle spasms, irregular or increased heart beat, extreme thirst and fainting.

19 Where high temperature is a problem, general ventilation must be provided. Cool drinking water and salt tablets should be available to employees in a lead dust free atmosphere.

#### **Noise**

20 Excessive noise can cause permanent hearing loss. Loud background noise (90 dBA) dulls human senses, including visual acuity, and increases accident rates. If the noise level around the machinery is higher than 90 decibels, those working on or near the equipment should be supplied with ear muffs. In situations where a worker must stay permanently near the equipment, a noise-insulated room should be provided from which he can watch the piece of equipment through a window.

21 Noise levels can be reduced by the separation and isolation of noisy operations, as well as impact reduction and vibration dampening by lamination or lining with acoustic materials. Mufflers on compressed air equipment

exhausts, and proper lubrication and maintenance of machinery will also reduce noise levels. Consideration of the noise producing characteristics should be given before purchasing new equipment.

#### **Sanitary facilities and requirements**

22 Good sanitary and washing facilities, including shower accommodations must be provided. Separate lockers for work and street clothes should be provided. Employees should be encouraged to wash up before eating. A separate lunchroom should be provided outside the work area.

#### **Medical examination**

23 Pre-employment and periodic medical examinations of all workers are recommended. Medical program should include biological monitoring for blood lead as described under paragraph for lead (para. 12 b).

#### **Training and education**

24 The education and training of employees in good safety practices is the responsibility of management. Employees should be instructed in safety and good working practices in all phases of their work. This should include regular training programs in the proper use of all equipment and machinery, safe lifting practices, location and handling of fire extinguishers, first aid procedures, the awareness of the danger of lead poisoning, and the use of personal protective equipment.

#### **Record keeping**

25 Management is required to keep records of all accidents and illnesses which have involved the employees in the plant. This information should be made available to the World Bank. An evaluation of injury and health data will assist the Bank to evaluate the effectiveness of its occupational health and safety program.



### 3.4.7 Summary of the Basel Convention and its consequences for lead-acid battery recycling

The implementation of recent decisions taken under the Basel Convention may influence the market for secondary lead smelting considerably, since many lead-acid batteries are transported across borders to be recycled elsewhere.

The consequences of the Basel Convention, in terms of environmental problems in developed and developing countries, are not clear yet. However, trainers may find it interesting to consider the impact of a restriction on transboundary transportation of hazardous wastes destined for recycling, and its effect on environmental quality.

*Compilation of press releases and decisions on the Basel Convention.*

The Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and their Disposal, adopted by the Conference of Plenipotentiaries in Basel in 1989, was developed under the auspices of the United Nations Environment Programme. The Convention passed into force during the First Meeting of the Conference of the Parties, held in Pririapolis, Uruguay, in 1992. The second meeting was held in Geneva, Switzerland, in 1994. During this meeting, it was decided to ban transboundary movement of hazardous wastes for final disposal from OECD to non-OECD states immediately. Exportation of hazardous wastes from OECD to non-OECD nations for recovery or recycling would cease by the end of 1997.

The Basel Convention represents a first step in defining the global means to reduce and strictly control the movements of hazardous wastes and to ensure that these wastes are disposed of in an environmentally sound manner. It provides realistic measures to strengthen the protection of the global environment from the possible harmful effects of the transboundary movements of hazardous wastes and their disposal. It focuses on

the protection of human health and the environment. It includes the obligation to reduce the generation of hazardous wastes to a minimum and to ensure that the sovereign right of each State to ban the import of hazardous wastes into its territory is observed. It also prohibits the export and import of hazardous wastes from and to non-Parties to the Convention unless such movement is subject to bilateral, multilateral or regional agreements or arrangements whose provisions are not less stringent than those of the Basel Convention. It requests that hazardous wastes should be disposed of as close as possible to their source of generation and that transboundary movement of hazardous wastes could only be allowed if it is carried out in accordance with the strict control system provided by the Convention, which includes prior informed consent by the importing country as well as by the transit country.

Transboundary movements of hazardous wastes carried out in contravention of the provisions of the Basel Convention are to be considered illegal traffic and a criminal act.

#### Implications for lead-acid battery recycling

Article I of the Basel Convention states that "... wastes that belong to any category contained in Annex I unless they do not possess any of the characteristics contained in Annex III ...," are regarded as hazardous wastes for the purposes of the Convention.

Lead, lead components and acids are regarded as hazardous wastes under the Convention. Lead and lead compounds are named under Y31, and

acidic solutions or acid in solid form are named under Y31 of Annex I. The characteristics of lead also comply with the characteristics listed under H11 and H12 of Annex III: Lead has toxic effects both delayed and chronic, and ecotoxic effects. Sulphuric acid possesses the characteristic described under H8 in Annex III: it causes severe damage when in contact with living tissue.

Final disposal operations of hazardous wastes from OECD countries in non-OECD countries which do not lead to the possibility of resource recovery, recycling, reclamation, direct re-use or alternative uses (Section A of Annex IV) is prohibited under the provisions of the Convention. This is also valid for lead-acid batteries.

Recycling/reclamation of metals and metal compounds and regeneration of acids is listed in Section B of Annex IV, stating the operations which may lead to resource recovery, recycling reclamation, direct re-use or alternative uses of hazardous wastes. Therefore the transboundary movement of lead-acid batteries for recycling is subjected to the regulations under the Basel Convention as of the end of 1997.

**Further information** Secretariat of the Basel Convention (SBC), Geneva Executive Center,  
15 chemin des Anémones, CH-1219 Châtelaine - Geneva, Switzerland.  
Tel: (41 22) 979 92 18. Fax: (41 22) 797 34 54.



## 3.5 Transparencies

**T**his section contains a set of transparencies which may be helpful to the trainer when explaining the concepts and principles of recycling of lead-acid batteries. The notes, accompanying every transparency, explain how to use the transparency. The trainer is encouraged to add transparencies to this set to suit his use.

The transparencies generally follow the sequence of the articles in *Sections 3.2-3.4*. Some transparencies can be used to illustrate certain exercises from *Part 5*. The trainer may want to add some of the tables and figures from *Part 3* and *Part 5* to this set of transparencies. It is left to the trainer to gather information on certain secondary lead-smelting processes and elaborate on its features during a course or workshop. You can find some references on secondary lead smelting processes in *Part 4*.

In case the presentation on lead-acid battery recycling is embedded in a course or workshop which is also emphasizing other environment related issues, please inquire at UNEP IE for additional, or related information and transparencies.

## **Acute Hazards of Lead**

- **Inhalation:**

*headache, nausea, abdominal spasm*

- **Ingestion:**

*headache, nausea, sore throat, abdominal spasm*

## **Effects of Long Term or Repeated Exposure**

- *Serious damage to the brain, kidneys, nervous system, and red blood cells*
- *Lead is especially harmful to children and embryos*

The margin between average lead-blood concentration and levels at which toxic effects may occur is small, particularly in children. Children tend to have higher blood-lead levels than adults. This is partly because they tend to put their hands and other things in their mouths, and partly because they absorb lead more easily. In addition, children are at further risk because the developing nervous system is more sensitive.



## **Important Sources of Long Term Exposure to Lead**

- **Lead emissions from (secondary) lead smelters**
- **Lead on the workflow**
- **Lead pipes and lead solder in drinking water systems**
- **Lead in petrol**
- **Lead in soldered cans for food products**
- **Lead from some paints**

Lead in drinking water systems, petrol, cans for food products and paints is being phased out in many countries. Other sources, such as lead glazes on cooking vessels, are generally no longer important in western countries. Check the status of lead phase-out in your country.

## **Measures to Prevent Exposure of Lead to Employees**

- **Wear protective masks**
- **Wear protective clothes and gloves**
- **Clean floors and process equipment regularly**
- **Service equipment and ventilation regularly**
- **No eating, drinking, or smoking on the work floor**
- **Wash after work**

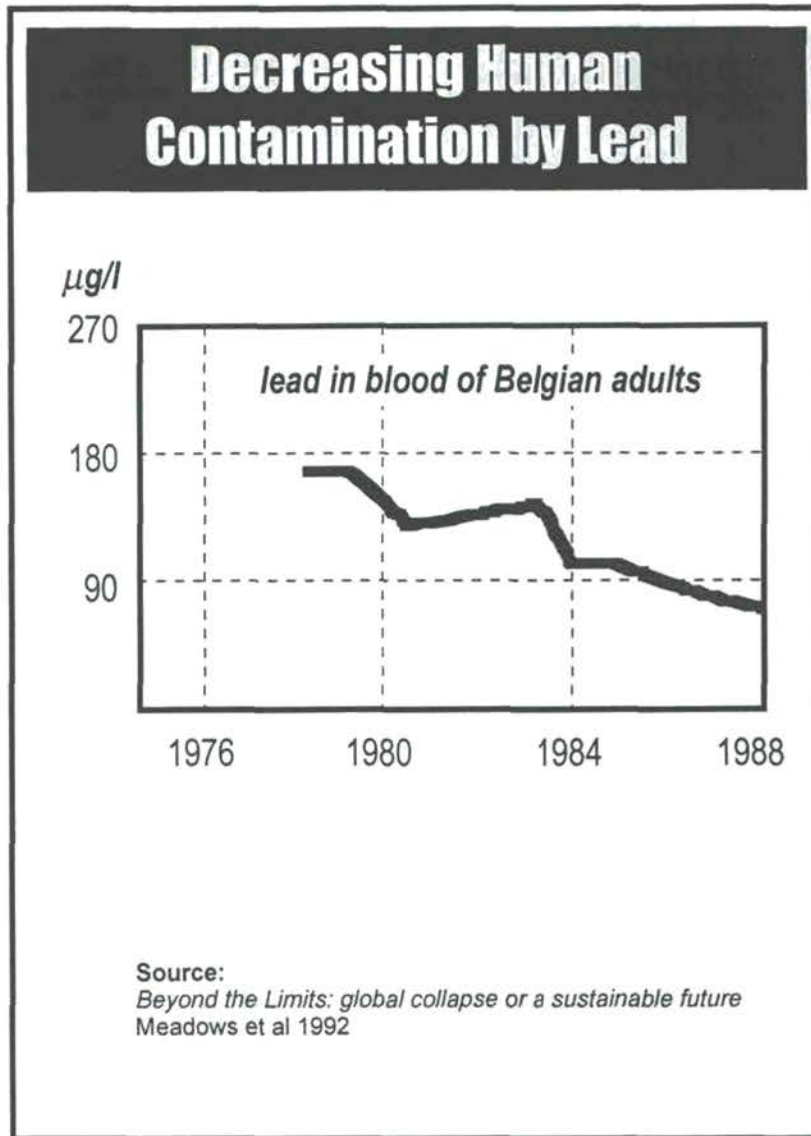
These measures to protect the employees at the working floor are daily practice in many secondary lead smelters. In addition, regular medical tests are being run to monitor the lead-blood level. The protective measures are generally taken to avoid ingestion of lead particles. Special training programmes for employees and work floor managers on how to protect themselves from exposure to lead are being run in many countries.



## Personnel Medical Care

Workers exposed to lead must have regular check-ups based on four main criteria:

- **Plombemia (Pb-B)**  
*determines the concentration of lead in the blood*
- **Hemoglobin (Hb)**  
*shows the final effect on the blood system*
- **Delta-aminolevulinic Acid (ALA-U)**  
*indicates the level of short-term impregnation*
- **Zinc-protoporphyrin (ZPP)**  
*shows the long-term biological effects.*

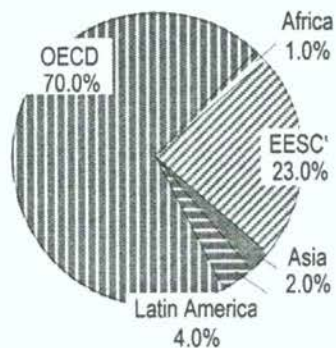


During past decades many countries have taken steps to reduce unacceptable human and ecosystem risks from exposure to lead. Among the most successful of these measures have been restrictions on the use of lead in certain products with significant exposure potential (for example, interior paint, petrol). The Belgium example shows the decrease of lead-blood concentration as a result of the restriction of lead use in petrol. Accompanying these measures have been actions to establish criteria for acceptable levels of lead in the environment to limit industrial emissions of lead to the environment, to control occupational exposures, and to identify ecologically based indices for determining populations at risk. Guidance for action has been given by international organisations, e.g.: International Register of Potentially Toxic Chemicals, United Nations Environment Programme (IRPTC/UNEP), Environmental Health Criteria 3: Lead (World Health Organisation, 1977), Environmental Health Criteria 85: Lead - Environmental Aspects (WHO, 1989), International Programme on Chemical Safety (IPCS), and Risk Reduction Monograph No. 1: Lead (OECD, 1993).

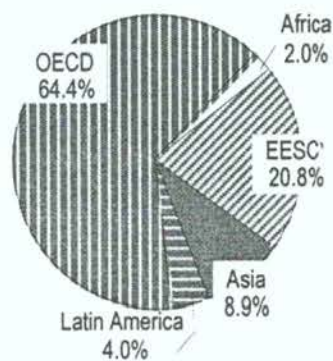


## World Demand for Lead

1970 4 502 000 tonnes



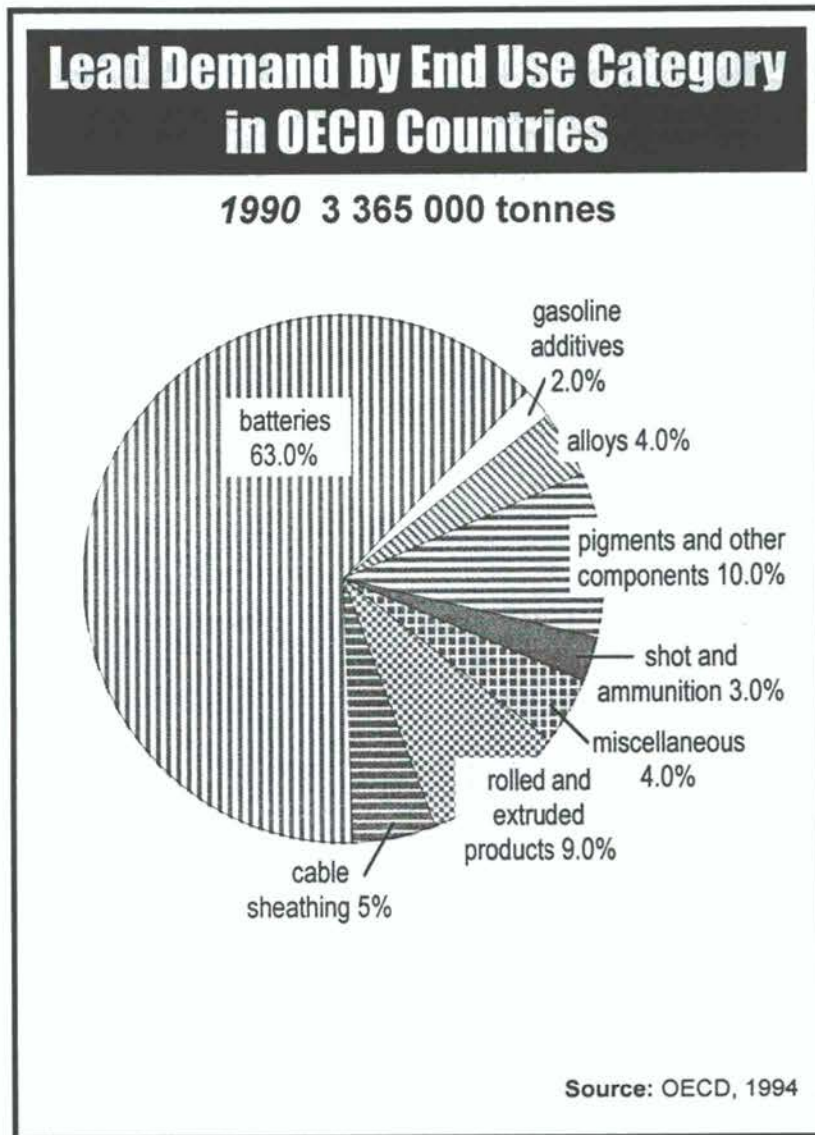
1990 5 627 000 tonnes



\*EESC: Eastern European and Socialist Countries

Source: OECD, 1994

This transparency shows the increase of lead production in the last twenty years. Lead demand is still increasing with an average of 1.2% per year.



This transparency gives a detailed description of the lead uses in OECD countries. Note that 63% of all lead uses in OECD countries are for lead-acid batteries. This amounts to 2,187,250 tonnes per year. This transparency can be used when discussing the exercise on the life cycle of lead (see Part 5 of this package).



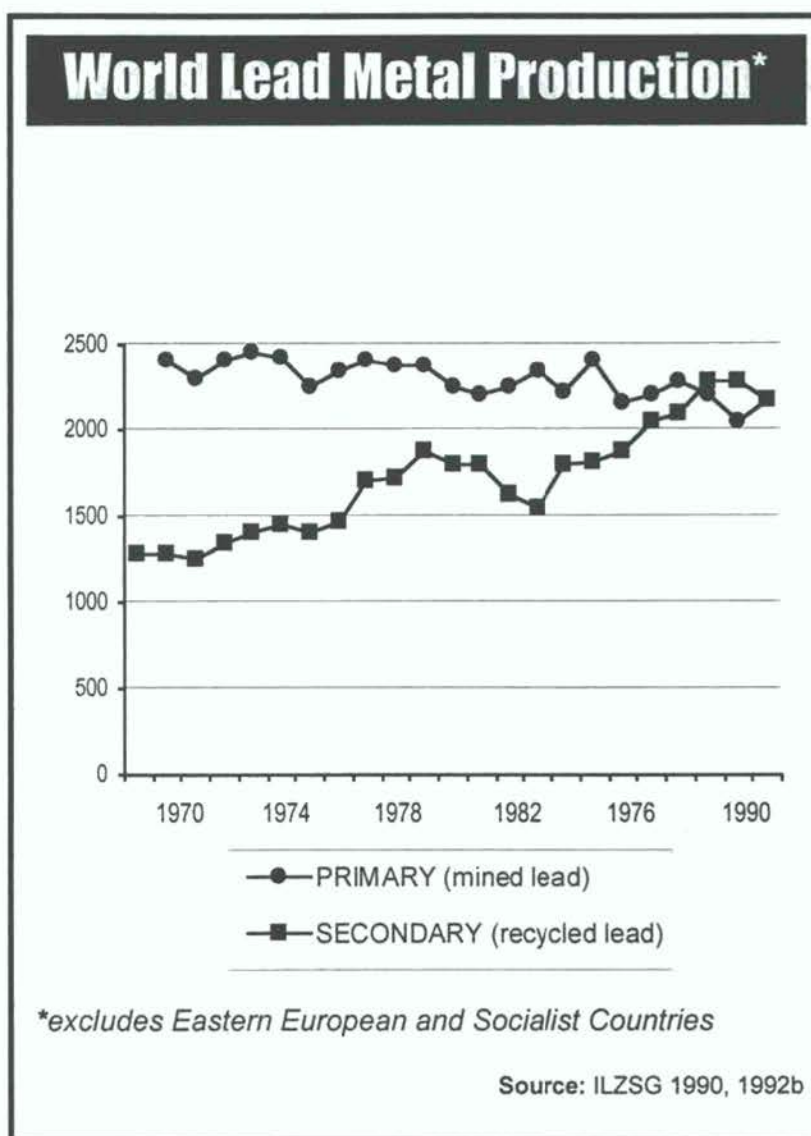
## London Metal Exchange

### Lead Price (real \$ 1991)



Source: EMR (1970-1991) (based on US GNP inflator)

Lead prices fluctuate considerably. Fluctuations in the price of lead has an important influence on lead-acid battery recycling. The lead-acid batteries will be stored longer when the prices are low, in anticipation of an increase in lead price.



While the production of primary lead has been steady over the last 20 years, the production of secondary lead has increased considerably. Effective recycling of lead-acid batteries plays an important role in attaining this high recycling rate, since more than 60% of all uses of lead are for lead-acid batteries.



## Recyclable and Non-Recyclable Applications for Lead

Recyclable	Non-Recyclable
Batteries	Gasoline additives
Roofing/flashings	Glass
Pipes	Plastics stabilizer
Cable sheaths	Shot/ammunition
Radiation shielding	Paint pigments
Window comes	Solders
Yacht keels	Ceramic glazes
Wheel weights	

Source Advances in Recovery and Recycling.  
Concepts and Technology.  
Recycling Congress.

Collected papers of the REC '93 International Recycling Congress.

This division of lead applications in recyclable and non-recyclable products may be used when designing the life cycle of lead in the working exercise on life cycles in Part 4 of this trainer package.

Refer also to the transparency explaining that more than 60% of all lead use is in lead-acid batteries and that more than 90% of all lead-acid batteries is recycled.

Refer also to the transparency concerning the OECD demand for lead by end use category, and see how much of all used lead can potentially be recycled.

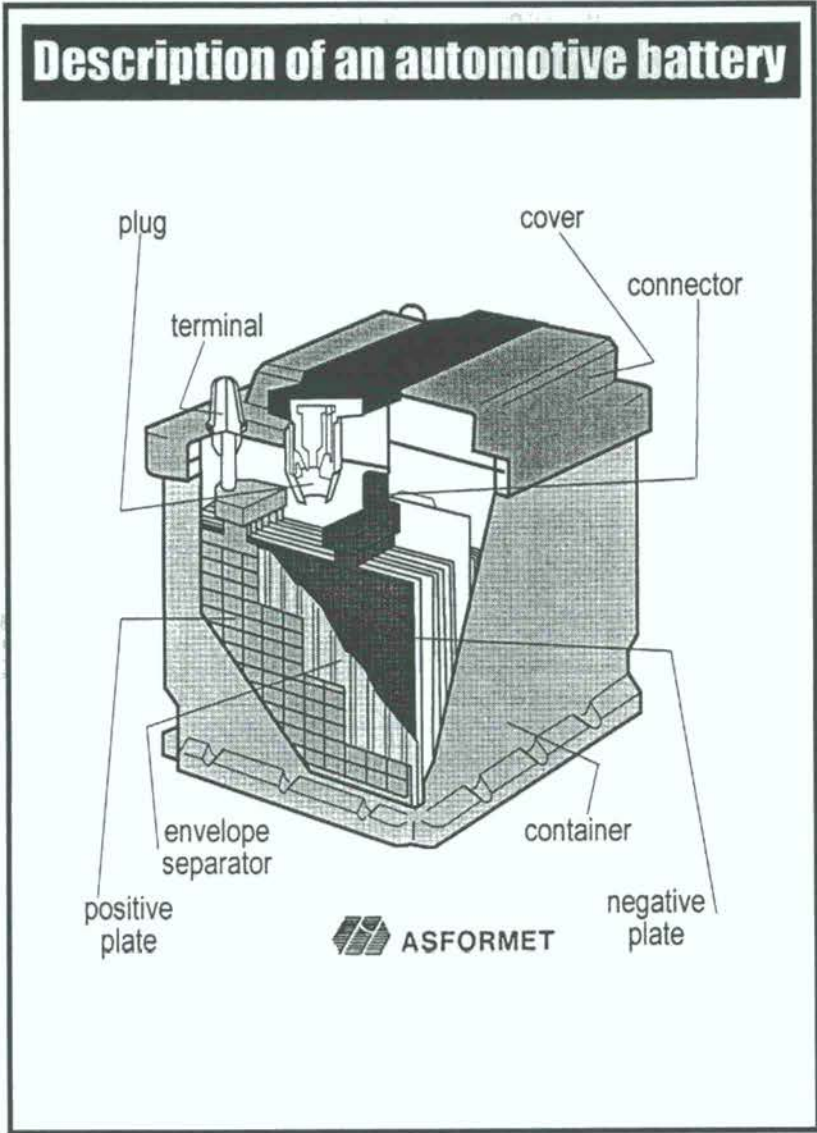
## Recovery of Lead Products

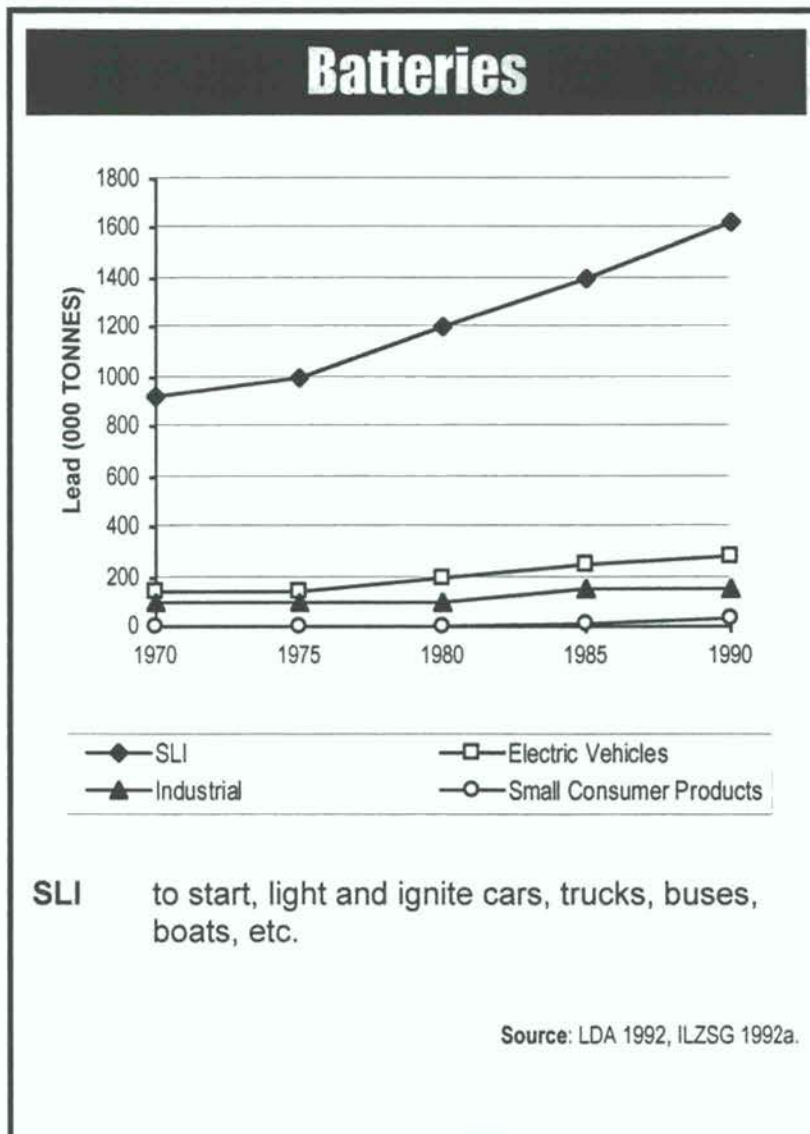
<i>Product</i>	<i>Product recovery</i>	<i>Life cycle (years)</i>
<b>Batteries</b>		
Automobile	+/- 90	3-4
Traction	+/- 100	4-6
Stationary	+/- 100	up to 10
<b>Sheet</b>	90-95	50-100
<b>Pipe</b>	70-80	50-100
<b>Cable sheathing</b>	50	40

Source Advances in Recovery and Recycling.  
 Concepts and Technology.  
 Recycling Congress.  
 Collected papers of the REC '93 International Recycling Congress.

This transparency indicates that lead-acid batteries have a relatively short life time and a high recycling rate. Due to this short life cycle, it is important that a high recycling rate is obtained in order to prevent uncontrolled disposal and losses into the environment.







This transparency shows that most batteries used are SLI batteries. SLI batteries, used for cars, buses, and trucks, are also the fastest growing compared to the other types of lead-acid batteries.



## Battery Recycling Rates in Some OECD Countries

	1986	1987	1988	1989	1990	1991
<i>Australia</i>						>90
<i>Belgium</i>	77					
<i>Canada</i>						93
<i>France</i>	80			90		90
<i>Germany FR</i>	83					>95
<i>Italy</i>	83					
<i>Japan</i>	93.3	92.5	95.2	93.8	92.2	
<i>Norway</i>						50*
<i>Sweden</i>						>100 <sup>e</sup>
<i>United Kingdom</i>	84					93
<i>United States</i>		88.6	91.0	95.3	97.8	

\* There are no lead recycling facilities in Norway. Scrap batteries are collected and then exported to other countries for recycling.

<sup>e</sup> = estimated

Source: OECD, 1994

This transparency shows that recycling rates for lead-acid batteries are very high, even though recycling is voluntary. Many OECD countries benefit from already existing infrastructures for metallic scrap recycling. Recycling rates can exceed 100 per cent when stored or stockpiled batteries are returned.

## Constituents of Used Lead-Acid Batteries

Component	Per Cent Weight
Metallic lead	17
Lead sulphate/oxide	50
Plastic	5
Acid	24
Residuals	4
<b>TOTAL</b>	<b>100</b>

## Chemical Additives to Lead-Acid Batteries

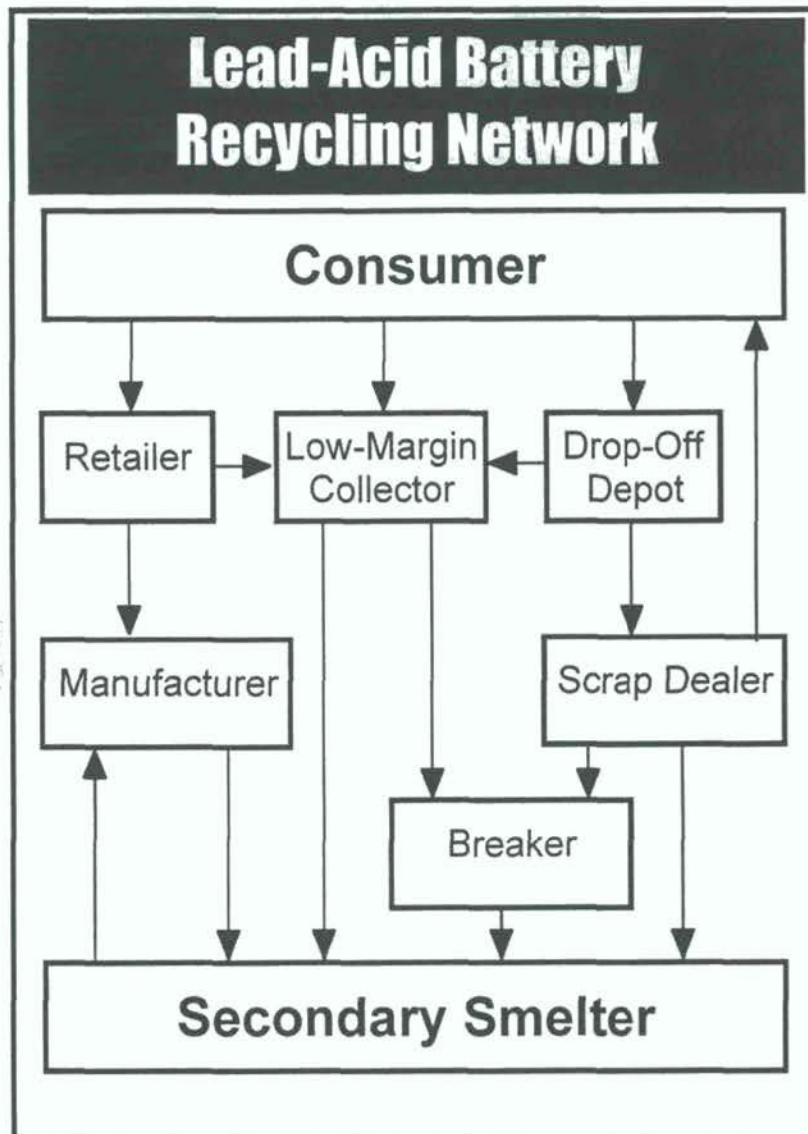
Additive	Concentration
Cadmium	0.1 - 0.14
Antimony	2.5 - 7.5
Arsenic	0.15
Tin	0.1 - 0.5
Copper	0.05

Source: Environment Canada, 1994

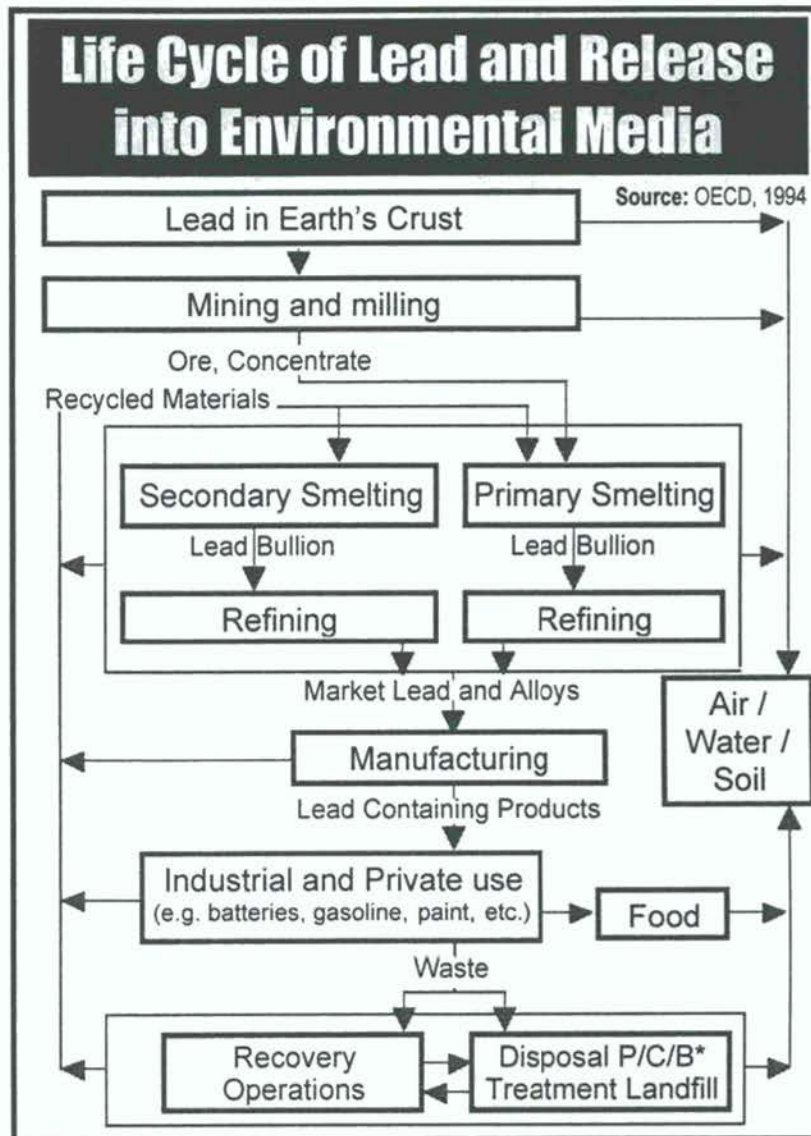
The plastic consists of three fractions: PVC, ebonite, and polypropylene. The residuals in the lead-acid batteries are mainly separators. The additives are used to increase anode hardness. An average SLI (Starting, Lighting, Igniting) battery weighs 17.2 kg and contains about 9.0 kg of lead, equally divided between anode and cathode. The electrolyte is generally 15-20% sulphuric acid (pH = 0.8) and is known to contain dissolved and particulate metals released from the electrolyte due to dissolution.

**NOTE:** Cadmium is not used as an additive in Europe. Cadmium forms toxic volatiles during smelting.





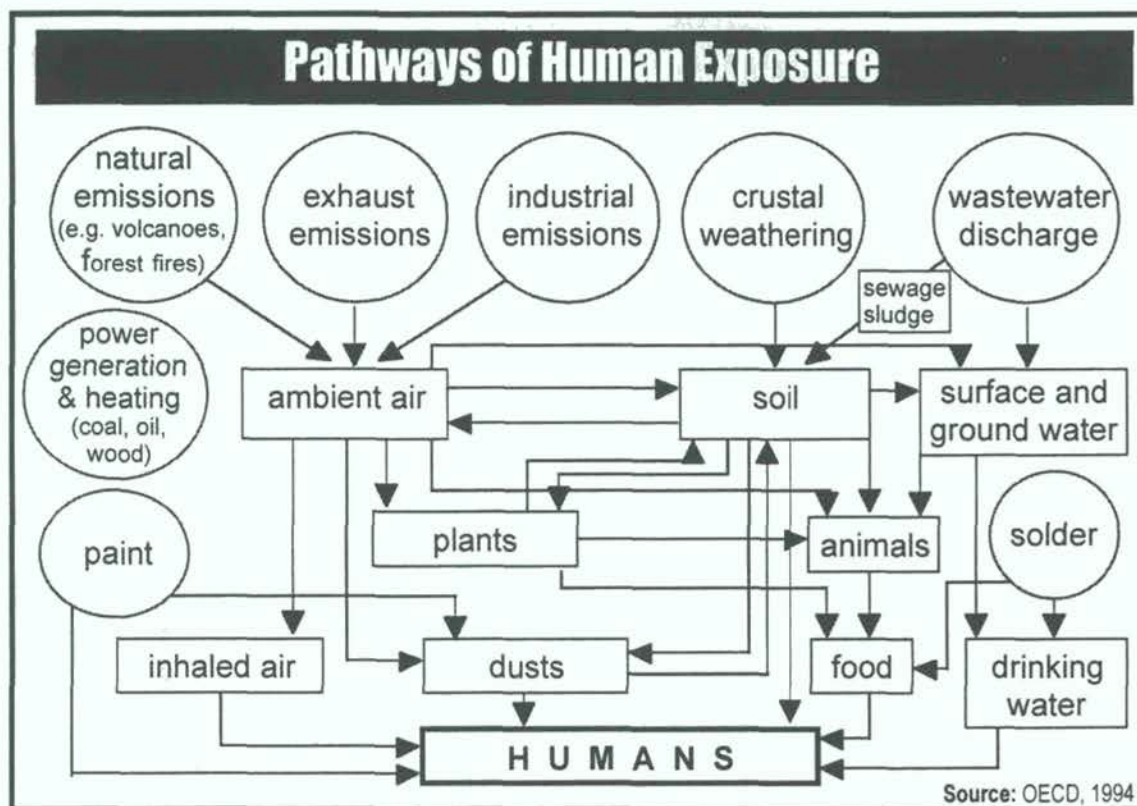
This transparency explains the channels through which the lead-acid batteries reach the secondary smelter.



\* Physical / Chemical / Biological

This transparency explains the life cycle of lead. Keep in mind that, on average, 60% of all lead is used for lead-acid batteries. This transparency can help explain the exercise on life cycle analysis.





This transparency explains the pathways through which lead reaches humans. This can be used when giving an introduction to lead-acid battery recycling, and explaining the dangers involved.

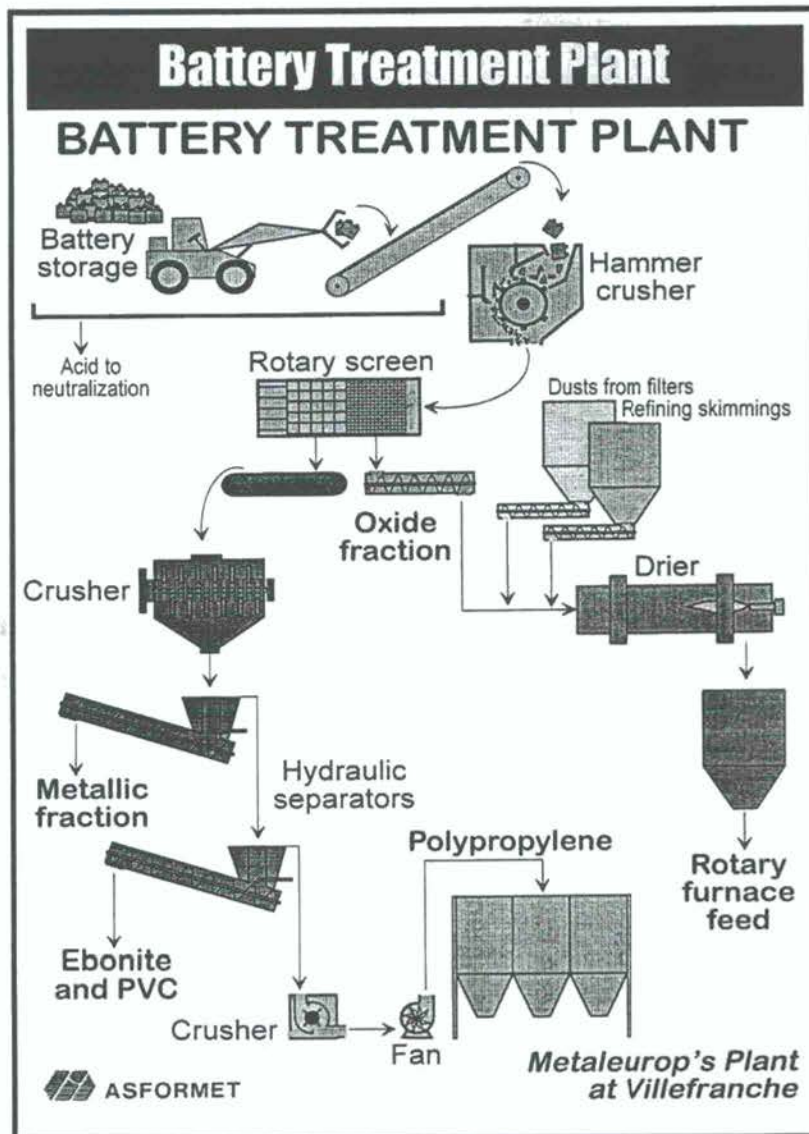
## Secondary Lead Smelters Overview

<i>Region</i>	<i>No. of Plants</i>	<i>Annual Capacity (000's Metric Tons)</i>
<i>Western Europe</i>	37	880.5
<i>Africa</i>	17	67.0
<i>North America</i>	47	1 311.0
<i>South America</i>	20	138.0
<i>Asia</i>	53	424.9
<i>Oceania</i>	4	41.0
<i>Eastern Europe</i>	9	275.0

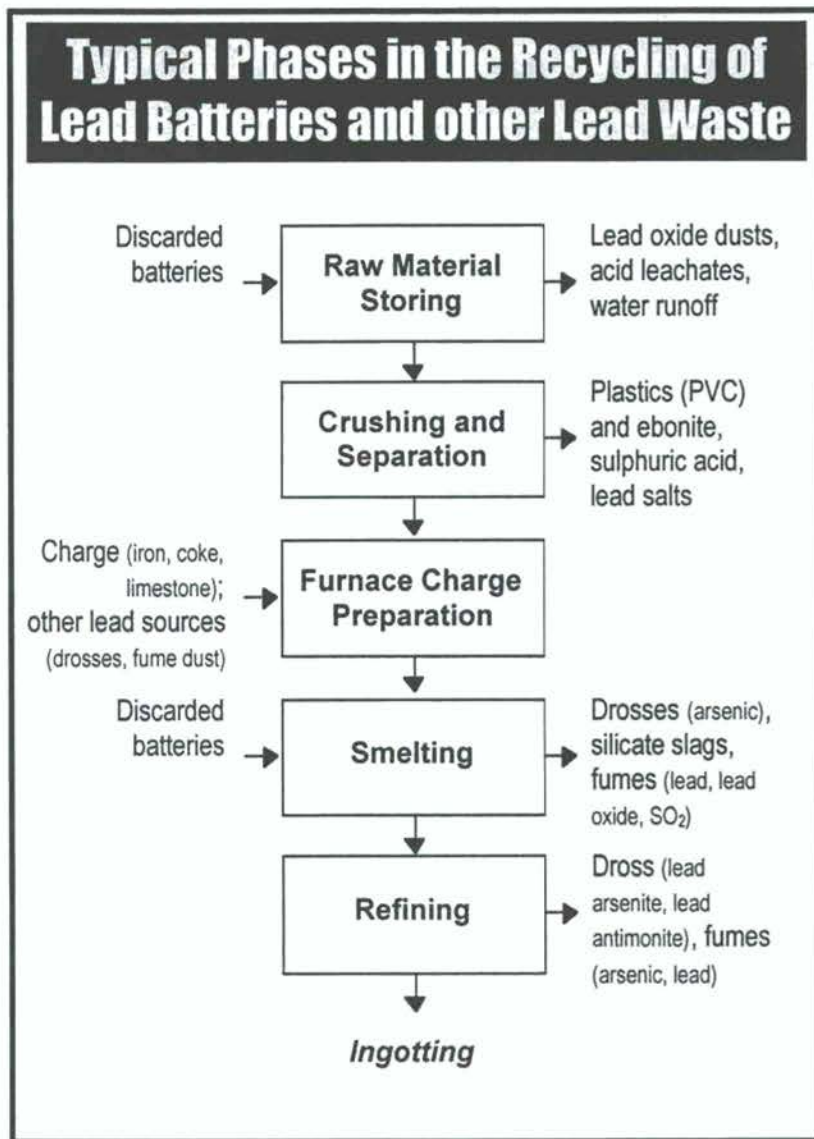
Source: International Lead and Zinc Study Group, 1994

This transparency gives an idea of the scale of lead recycling worldwide as of March 1994. It should be noted that small plants with capacities for lead smelting of less than 1,000 metric tons per year have been omitted from this transparency. Most lead-smelters range in capacity from 10,000 to 30,000 metric tons per year. Keep in mind that not all batteries are consumed and recycled in the same country. Thus, rates of consumption and smelting may not be the same in a given country. This will change with the enforcement of the Basel Convention on transboundary movement of hazardous wastes. The consequences of the Basel Convention for the transboundary movement of used lead-acid batteries has not been dealt with in this trainer package. However, the trainer may want to address this issue separately.



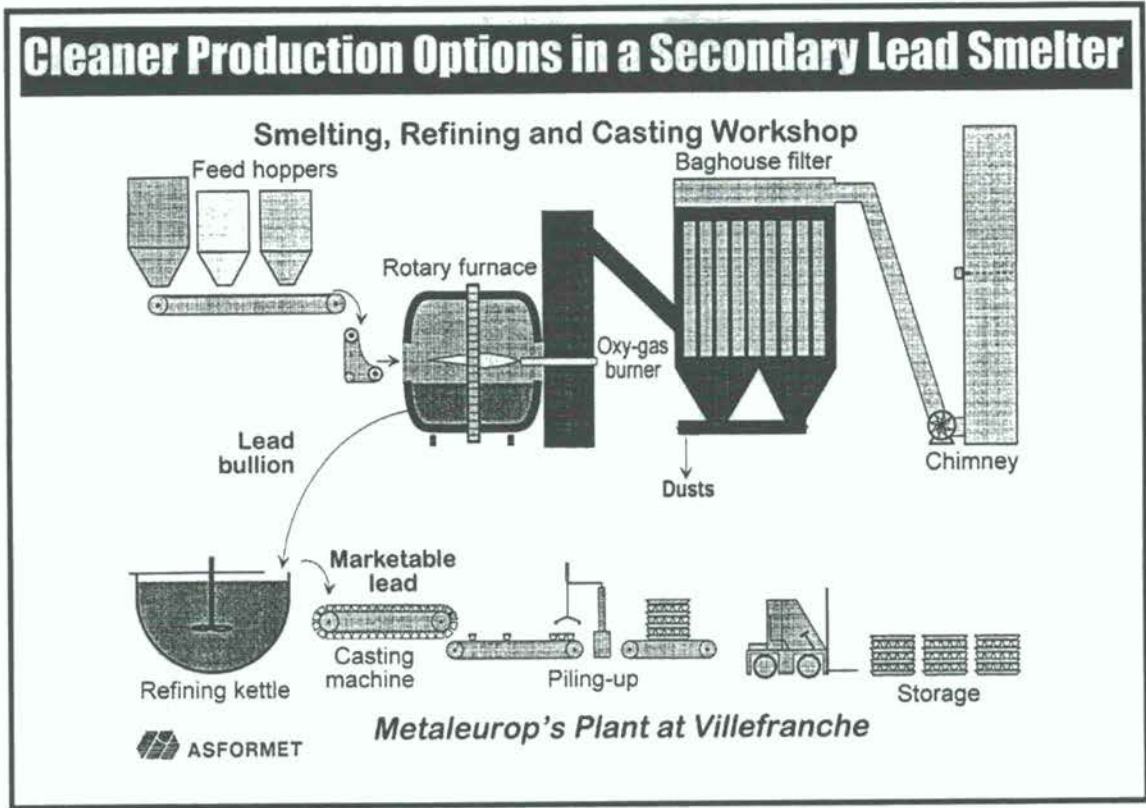


This diagram is typical of many plants. For a more complete overview of various technologies, readers should refer to the recent UNEP IE report on the subject.



This is a flow diagram with the possible inputs and outputs of a battery recycling process. These inputs and outputs may differ depending on the technologies used. The following transparencies explain the process in more detail, distinguishing three phases: wrecking, smelting, and refining.





## Secondary Lead Smelting

### 1 Wrecking

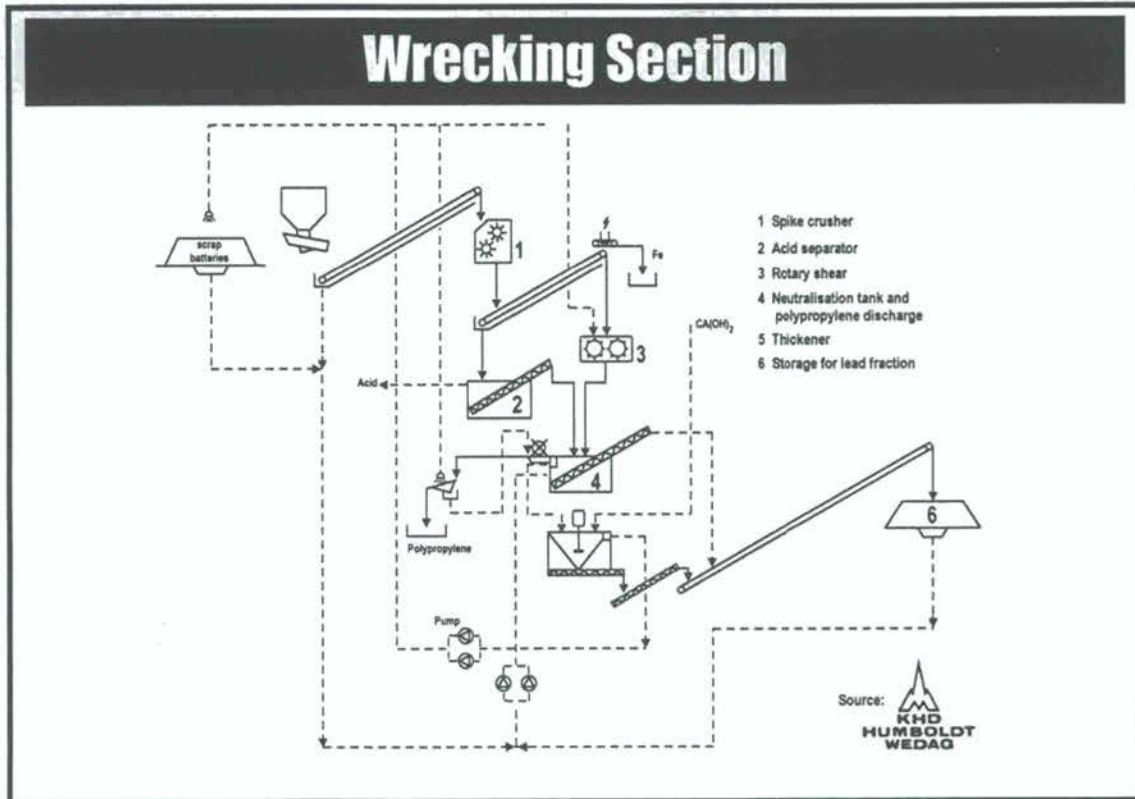
*Separation of plastics and lead-bearing material by flotation into:*

- Lead paste in decanted slime
- Grid scraps of lead alloy, containing antimony, arsenic and tin
- Plastics (PVC, polypropylene, ebonite)
- Liquid effluents (battery acids and lead oxides)

The battery recycling process mainly consists of three phases: wrecking, smelting, and refining. The output of the wrecking process depends on the technologies being used and the market for the recycled products (see background papers). In some recycling facilities, the wrecking phase did not exist and batteries were discharged directly into the smelter. This practice results in serious air pollution. Fortunately, this is no longer current practice.

Several wrecking sections are discussed in the background papers and in the exercises on the lead-acid battery recycling facility.





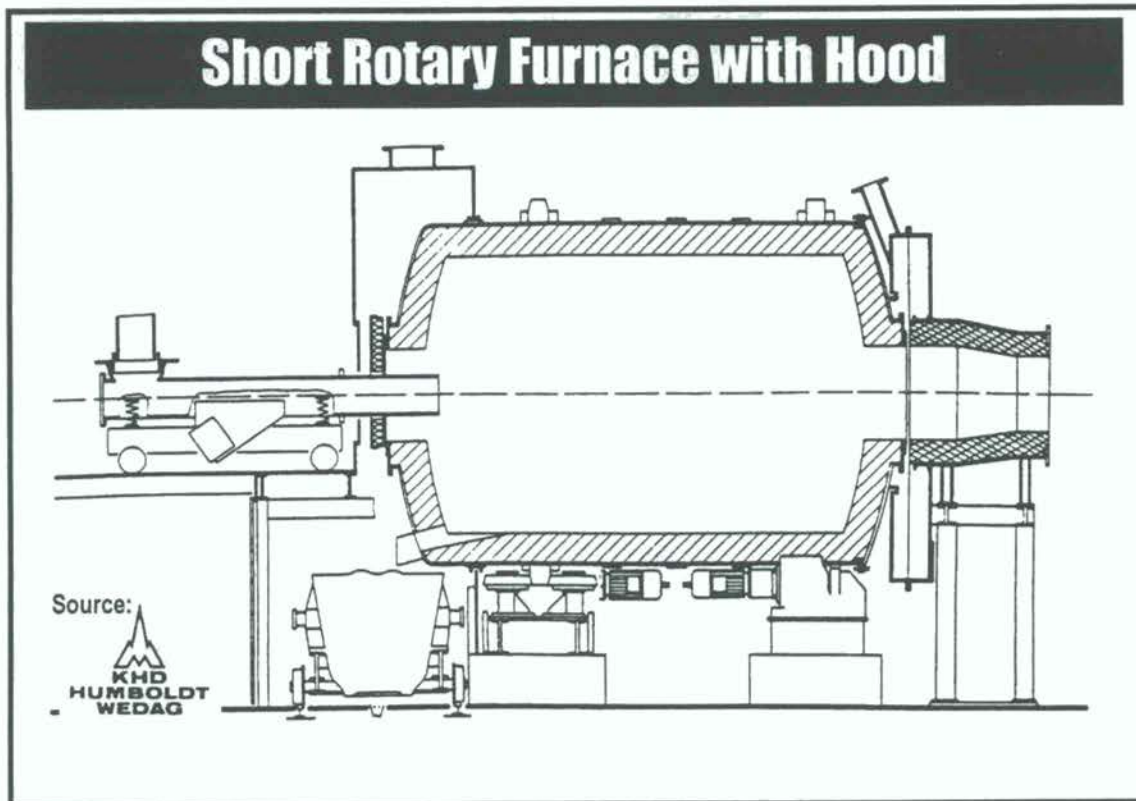
## Secondary Lead Smelting

### 2 Smelting

- Melting of solid fractions and reduction of lead paste (+/ – 1250°C)
- Burnout of organic contaminants (e.g. rubber, PVC, polypropylene, paper, etc.)
- Removal of drosses, containing iron, arsenic, antimony and tin

Most current lead smelters separate the plastics fractions from the lead fraction during the wrecking section. The plastic is hardly used as a fuel any more during the smelting phase. Reagents (soda, CaO, SiO<sub>2</sub>, and Fe-chips) are added in order to reduce the lead oxide and the lead sulphates (lead paste) to mineral lead.

Some smelting operations are preceded by desulphurization to reduce the generation of SO<sub>2</sub>. There are many different furnaces which can be used for the smelting process. Some of the most commonly used are: the *rotary reverberatory* furnace, the *blast* furnace, and the *stationary reverberatory* furnace.



This transparency gives a schematic presentation of a typical smelting section. The case-study on the lead-acid battery recycling facility in Part 5 of this trainer package also refers to this typical smelting operation.



## Secondary Lead Smelting

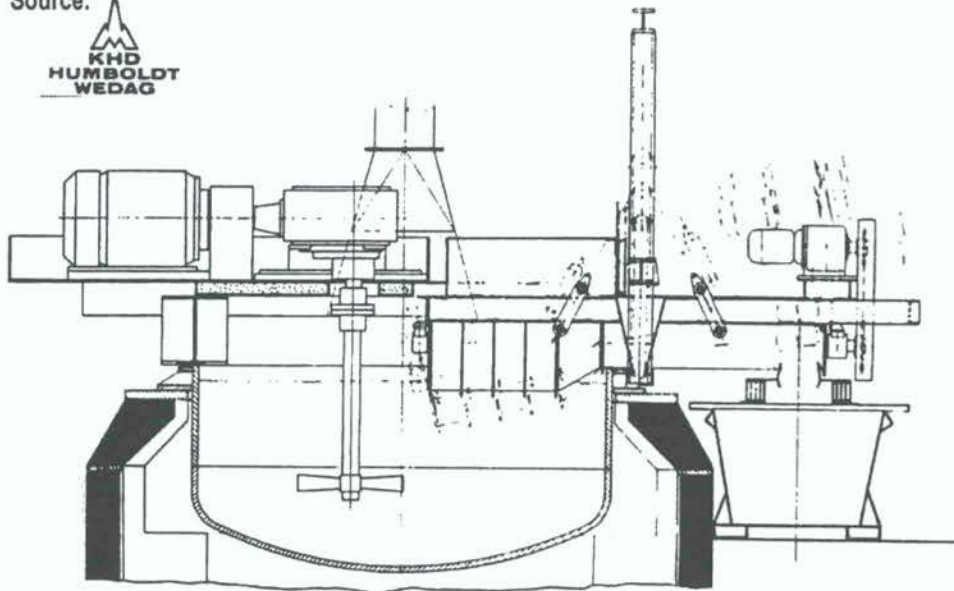
### 3 Refining

- **Remelting** of the smelted lead (350–600°C).
- **Alloying** antimony, tin, arsenic and copper.
- **Refining** through:
  - [a] removal of copper and antimony to produce soft lead*
  - [b] removal of arsenic and copper to produce hard lead.*

Remelting, alloying, and refining is carried out batch-wise in pot and kettle furnaces. Depending on the demand, the products of refining are either *hard* or *soft lead*. For copper removal, the temperature of the molten lead is allowed to drop to 320°C and sulphur is added.

## Kettle with Hood, Agitator and Removing Screw

Source:



This transparency gives a schematic presentation of a typical refining section. The case-study on the lead-acid battery recycling facility in Part 5 of this trainer package also refers to this typical refining operation.

## Cleaner Production Options in a Secondary Lead Smelter

### *Example*

<i>Unit Operation</i>	<i>Cleaner Production Action and Environmental/Product Quality Benefit</i>	<i>Cost</i>	<i>Financial benefit</i>	<i>Payback Period</i>
<b>Conversion of Scrap Lead into Cast Panels:</b>	Cover slag and dust piles and clean smelting room – reduces worker exposure to lead and lead dust	\$500	\$9,700	3 weeks

These options were produced as part of a US AID project, aimed at introducing cleaner production approaches and measures into Tunisian industries. Of course, the options presented here are not necessarily feasible or possible in all secondary lead smelters.

Cleaner production measures are pro-active, i.e. they aim to prevent pollution rather than to clean it up at the 'end-of-the-pipe'. The cleaner production approach, promoted by UNEP IE, is worth considering in all industries, including secondary lead smelters. There is a Training Resource Package available on cleaner production from UNEP IE.





## *Part 4*

# Information Sources

<b>4.1</b>	<b>Introduction .....</b>	<b>IV:3</b>
<b>4.2</b>	<b>Sources of information .....</b>	<b>IV:3</b>
<b>4.3</b>	<b>Documents on lead and lead-acid batteries recycling .....</b>	<b>IV:5</b>
<b>4.4</b>	<b>Handbooks on chemicals, humans and the environment....</b>	<b>IV:7</b>
<b>4.5</b>	<b>Audiovisuals .....</b>	<b>IV:8</b>
<b>4.6</b>	<b>Some background documents on the environment .....</b>	<b>IV:10</b>

# 4 Information Sources

## 4.1 Introduction

**P**art 4 contains some references to information sources on lead-acid battery recycling in particular, and on recycling in general. It also contains information about:

- background documents on lead-acid battery recycling,
- handbooks on chemicals, humans and the environment,
- audiovisuals.

A reference list on general environment related issues is also included, in case the trainer requires more information on the most important environmental issues of today.

## 4.2 Sources of information

### United Nations Environment Programme: Industry and Environment (UNEP IE)

UNEP IE provides a query response service, answering technical and general requests for information and documentation related to industrial pollution.

*Further information:*

UNEP IE, 39-43 Quai André Citroën,  
75739 Paris, Cedex 15, France.

Tel (33 1) 44 37 14 50; Fax (33 1) 44 37 14 74.

### UNEP International Register of Potentially Toxic Chemicals (IRPTC)

Provides information on chemicals, waste disposal and discharge regulations, including the current international list of banned or severely restricted chemicals.

*Further information:*

UNEP IRPTC, Palais des Nations,  
CH 1211 Geneva 10, Switzerland.

Tel (41) 22 979 91 11; Fax (41) 22 797 34 60.

### UNEP/WHO/ILO International Programme for Chemical Safety (IPCS)

Toxicological information on chemicals.

*Further information:*

IPCS, c/o World Health Organization,  
CH 1211 Geneva 27, Switzerland.

Tel (41) 22 791 11; Fax (41) 22 791 07 46.

### United Nations Industrial Development Organization (UNIDO).

UNIDO provides an information database: the Industrial and Technological Information Bank (INTIB) of UNIDO.

*Further information:*

INTIB, UNIDO, PO Box 300,  
A-1400 Vienna, Austria.

Tel (43 1) 21131/3705; Fax. (43 1) 230 7584.

### Battery Council International

111E Wacker Drive, Suite 600, Chicago,  
IL 60601, USA. Tel (1 312) 644 6610.

### EP3 (Environmental Pollution Prevention Project Clearinghouse)

The EP3 Clearinghouse is an information service that collects, compiles, and assesses technical reports, books, journal articles, and other materials on pollution prevention, and disseminates them to businesses and governments in developing countries. The Clearinghouse also provides information on a broad range of environmental issues, and works with INFOTERRA/USA to obtain current worldwide environmental information.

*Further information:*

**EP3 Clearinghouse**, 1530 Wilson Boulevard,  
Suite 900, Arlington, VA 22209-2406, USA.

Tel (1 703) 351 4004; Fax (1 703) 351 6166.



**INFOTERRA** 3404, US EPA, 401 M Street,  
S.W. Washington, D.C. 20460, USA.  
*Tel* (1 202) 260 5917; *Fax* (1 202) 260 3923.

**Eurométaux**

European association representing the metal industries in Europe.

*Further information:*

Eurométaux, 6th Floor,  
Avenue de Broqueville 12,  
B-1150 Brussels, Belgium.  
*Tel* (32 2) 775 63 11; *Fax* (32 2) 779 05 23.

**European Directory of Hazardous Waste Management 1993/94** [1993] C. Newsome (Ed.)

This directory contains descriptions and addresses of European and Scandinavian companies active in hazardous waste management.

*Further information:*

Graham & Trotman Ltd., Sterling House,  
66 Wilton Road, London SW1V 1DE,  
United Kingdom.

**International Lead Zinc Research Organization, Inc.**

*Further information:*

2525 Meridian Parkway, PO Box 12036,  
Research Triangle Park, N.C. 27709, USA.  
*Tel* (1 919) 361 4647; *Fax* (1 919) 361 1957.

**International Lead and Zinc Study Group**

Metro House, 58 St. James's Street,  
London, SW1A 1LD, UK.  
*Tel* (44 71) 49 99 373; *Fax* (44 71) 49 33 725.

**MetalEurop**

A corporation which produces lead, germanium, indium, and zinc. Active in lead, zinc, and polypropylene recycling.

*Further information:*

Metaleurop S.A., 58 rue Roger Salengro,  
94126 Fontenay-sous-Bois Cedex, France.  
*Tel* (33 1) 43 94 47 00; *Fax* (33 1) 43 94 03 81.

**OECD Environment Directorate**

Environmental Health and Safety Division

This division prepared a number of documents on risk reduction activities for specific chemicals or groups of chemicals. The first *Risk Reduction Monograph* was on lead (see background documents).

*Further information:*

2, rue André Pascal,  
75775 Paris Cedex 16, France.  
*Fax* (33 1) 45 24 16 75.

**"Spravochnik: ekologicheskiye organizatsii na territorii byivshevo SSSR"**

This handbook on ecological organisations in the former Soviet Union is published by The Institute for Mass Political Movements and RAU-Press. It gives contact names, the purpose of the organizations, and ways of contacting of over 800 groups and institutions.

*Further information:*

MIPP Company, 2225 Benson Avenue,  
Brooklyn, NY 11214, USA.  
*Tel* (1 718) 373 3173.

**The International Occupational Safety and Health Information Centre (CIS)**  
of the International Labour Organization

*Further information:*

CIS, International Labour Organization,  
4 route des Morillons,  
CH 1211 Geneva 22, Switzerland.  
*Tel* (41 22) 799 67 40; *Fax* (41 22) 798 86 85.

**The Regional Environmental Center for Central and Eastern Europe (REC)**

Promotes cooperation among environmental groups and interests in the region, acts as a catalyst for developing solutions to environmental problems, and promotes development of a civil society. REC primarily supports environmental NGOs, cooperates with local authorities, national governments, academic institutions, and the private sector.

*Further information:*

Miklos ter 1, 1035 Budapest, Hungary.  
*Tel* (36 1) 250 3401; *Fax* (36 1) 250 3403.

**Unicorn Publications**

A nonprofit environmental publishing house in Kiev. Unicorn Publications provides readers in Ukraine and other countries of the former Soviet Block with books and briefings on topics related to ecological economics, resource conservation, mass transportation, renewable energy, organic agriculture, etc. Unicorn translates classics of western environmental literature into Ukrainian and Russian, adapting them to local conditions and culture and making them available through Unicorn contacts in Germany, the Netherlands, UK, USA, Austria and Slovakia.

*Further information:*

Andriy Glazovoy (044) 442 3171;  
John Spaulding (044) 213 7946.



## 4.3 Documents on lead and lead-acid batteries recycling

### **Advances in Recovery and Recycling: Concepts and Technology Volume III** [1993]

M.E. Henstock; H.R. Skov (Eds.)

*Collected papers of the REC '93 International Recycling Congress, Geneva, Switzerland.*

Volume III of the collected papers contains a paper explaining the recycling of lead. Since more than 50% of all recycled lead originates from used lead-acid batteries, this is an interesting article which introduces the reader to recycling schemes and the technology of lead smelting.

#### *Further information:*

Hexagon Ltd., P.O. Box 80,  
DK-1003 Copenhagen K, Denmark.

### **Guidelines for the Management of Used Lead-Acid Batteries in Canada** [1993]

This publication contains a description of the current battery management process in Canada, together with a set of recommended practices for promoting consistency in the management of used lead-acid batteries across Canada.

#### *Further information:*

Environment Canada, Hazardous Waste Division, Office of Waste Management, Place Vincent Massey, 12th Floor, 351 St. Joseph Blvd., Hull, Quebec, K14 0H3, Canada.

### **Hazardous Waste: Detection, Control, Treatment Part B** [1988] R. Abbou (Ed.)

*Proceedings of the World Conference on Hazardous Waste, held in Budapest, Hungary, on October 25-31, 1987.*

The proceedings contain an article on a modern and low-pollutant secondary lead smelter to be set up in Hungary, and an incineration feasibility study for battery plant trash and crushed rubber battery cases.

#### *Further information:*

Elsevier Science Publishers BV,  
Sara Burgerhartstraat 25, P.O. Box 211,  
1000 AE Amsterdam, The Netherlands.

### **Lead Astray: the poisonous lead battery waste trade** [1994] Greenpeace

This publication contains basic information on the lead trade and recycling practices. It also discusses the impact of the lead trade in developing countries. The discussion is based on research done on lead recycling practices and the environmental and health impacts of lead recycling in six developing countries.

#### *Further information:*

Greenpeace, Toxic Trade Publications,  
1436 U St NW. Washington,  
D.C. 20009, USA.

Tel (1 202) 462 1177; Fax (1 202) 462 4507.

### **Productivity and Low Waste Technology for Reprocessing Battery Scrap** [1989]

K.F. Lamm; A.E. Melin.

In: *Productivity and Technology in the Metallurgical Industries*. The Minerals, Metals and Materials Society.

### **Recycling Lead And Zinc:**

#### **The Challenge of the 1990s** [1991]

*Proceedings of the conference organized by the International Lead and Zinc Study Group Sub-Committee on Recycling, held in Rome, Italy, on 11-13 June 1991.*

The proceedings contain papers covering the principal aspects of recycling:

- trends in world supply and demand for lead and zinc;
- the role of the secondary sectors;
- the extent of the recovery;
- existing and developing recycling technologies;
- environmental and health concerns and the regulatory framework.

#### *Further information:*

International Lead and Zinc Study Group,  
58 St James's Street, London SW1A 1LD, UK.  
Tel (44 71) 499 9373; Fax (44 71) 493 3725.

**Risk Reduction Monograph No. 1: Lead**

***Background and national experience with reducing risk*** [1993]

This document contains information on

- the commercial life cycle;
- the environmental life cycle;
- links between sources and targets;
- risk reduction and control measures and their cost/effectiveness;
- conclusions that can be drawn regarding the effectiveness of risk reduction measures, the identification of major exposures that need to be addressed to help risk reduction, and critical information gaps.

*Further information:*

OECD Environment Directorate,  
Environmental Health and Safety Division,  
2, rue André Pascal, 75775 Paris Cedex 16,  
France.

*Fax* (33 1) 45 24 16 75.

**States' Efforts to Promote**

**Lead-Acid Battery Recycling** [1992]

This report is written to help the US EPA determine how EPA and States can most effectively promote lead-acid battery recycling. It describes the car battery recycling chain, characterizes State lead-acid battery recycling requirements, and reviews the effectiveness of State laws in promoting lead-acid battery recycling.

*Further information:*

US EPA,  
Office of Policy, Planning and Evaluation,  
Programme Evaluation Division  
*Mailcode:* PM-223Z  
Waterside Mall (WSM), 401 M Street S.W.,  
Washington, D.C. 20460, USA.  
*Tel* (1 202) 260 5333.

**Storage Battery Technical Service Manual** [1982]

*Published by Battery Council International.*

This manual gives full information on how to handle new batteries, from transportation to servicing.

*Further information:*

Battery Council International, Headquarters,  
111 East Wacker Drive Chicago, ILL 60601.  
*Tel* (1 312) 644 6610.

**World Directory: Secondary Lead Plants** [1994]

*International Lead and Zinc Study Group (ILZSG).*

This publication contains information on all small, medium and large sized lead smelters and refineries operating solely or partly from concentrates and bullion.

*Further information:*

ILZSG, Metro House, 58 St. James's Street,  
London, SW1A 1LD, UK.  
*Tel* (44 71) 499 9373; *Fax* (44 71) 493 3725.



## 4.4 Handbooks on chemicals, humans and the environment

### Chemical Hazards in the Workplace [1989]

R.M. Scott.

### Environmental Health Criteria: *Lead* [1983] and *Lead: Environmental Aspects* [1989]

World Health Organization, International Programme on Chemical Safety (IPCS).

#### *Further information:*

WHO, Distribution and Sales Services,  
1211 Geneva 27, Switzerland.

### IARC Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Humans: *Some metals and metallic compounds Volume 23* [1980]

World Health Organization (WHO),  
International Agency for Research on Cancer.

This publication contains data on lead, including the production processes and uses of different lead appliances.

#### *Further information:*

WHO, Distribution and Sales Services,  
1211 Geneva 27, Switzerland.

### Handbook on the Toxicology of Metals

2nd Ed [1986]

L. Friberg; G.F. Nordberg; V.B. Vouk.

### Health and Environmental Lead in Australia [1987]

Australian Academy of Science.

### Occupational Medicine: Principles and Practice

[1988] Carl Zenz (Ed.)

### Plomb & Sante dans l'Industry: Proteger les

travailleurs – Pourquoi, comment? [1990]

In this book you will find methods to actively protect employees from lead exposure, the required medical surveys, and ways to recognize symptoms of lead-poisoning. The book is available in French.

#### *Further information:*

Centre d'Information du Plomb,  
Péripole 118, 52 rue Roger Salengro,  
94126 Fontenay-Sous-Bois Cedex.  
Tel (33 1) 43 94 48 80.

### Proctor and Hughs' Chemical Hazards of the Workplace [1991]

### 4.4.1 Journals related to lead

#### Batteries International.

Quarterly published by

*Batteries International Ltd.*

#### *Further information:*

Batteries International Ltd.,  
Aberdeen House, Headley Road, Grayshott,  
Hindhead, Surrey GU26 6LA, UK.  
Tel (44 428) 605 536; Fax (44 428) 606 339.

#### Journal of Power Sources: The International Journal on the Science and Technology of Electrochemical Energy Systems

#### *Publisher:*

Elsevier Sequoia S.A., P.O. Box 564, 1001  
Lausanne, Switzerland.



## 4.5 Audiovisuals

### **BSB Recycling Zentrum [1989]**

Video on the Blei- und Silverhütte Braubach, 16 min., in German. This video explains the processes and technologies used in the BSB hütte to recycle lead-acid batteries and recover their constituents with the least environmental impacts.

#### *Further information:*

Blei- und Silber hütte Braubach,  
BSB Recycling GmbH, D-5423 Braubach.

### **Reduce worker exposure to lead**

A video and a compliance manual are available to help operators comply with US Occupational Safety and Health Administration lead standards. The video explains regulatory requirements, measurement options, techniques for assessing exposure levels and compliance methods. The manual includes detailed background information, major requirements, 'fill in the blank' compliance forms, and a glossary of terms. Marshall Productions, Trenton, N.J.

#### *Further information:*

Ask for 'Free product information No. 251',  
Chemical Engineering,  
Reader Service Management, PO Box 5273,  
Pittsfield, MA 01203-9916, USA.

### **Malette Pédagogique**

This is a train-the-trainer toolkit developed by Metaleurop (available in French). It contains educational material for employees in industry on how to protect themselves from lead exposure, including a video, brochures, folders, posters, a user's guide, and case-studies. It costs FF700. Metaleurop also organizes a two day train-the-trainer programme on how to protect personnel from lead exposure. The seminar costs FF3200.

#### *Further information:*

Metaleurop S.A., 58 rue Roger Salengro 94,  
126 Fontenay-sous-Bois Cedex.  
Tel (33 1) 43 94 47 00; Fax (33 1) 43 94 03 81.



IChemE has an international reputation for providing high quality, effective safety and environmental training solutions using video, slide, open learning and computer-based techniques. We draw on experts throughout industry, the regulatory bodies, the legal profession and academia to ensure that our training packages are both high quality and relevant.

## 4.5.1 Environmental packages

### ENVIRONMENTAL AWARENESS

#### **Package E02**

Understanding is the key to effective environmental improvements - both through certified standards and effective policy implementation. This package gives a thorough grounding in environmental awareness. The case studies cover: environmental law; global issues; corporate issues; and waste minimization.

### AQUEOUS EFFLUENTS

Volume 1: awareness and treatment strategies

#### **Package E01**

Engineers learn how to assess and deal with effluent problems; senior management gain a sound technical and legal grounding; and operators learn why compliance is important. Seven case studies demonstrate how effective treatment strategies save money whilst benefiting the environment. And the technical guidance covers: characterisation of effluents; treatment strategy; safety; unit operations; and costs.

Volume 2: measurement and monitoring

#### **Package E013**

Trainees learn how to measure and monitor effluents, ensuring compliance and reducing treatment costs.

### AIR EMISSIONS

Volume 1: key issues

#### **Package E03**

This package provides comprehensive coverage of generic air pollution issues and technologies, backed up with detailed sections on sources and types of emissions, atmospheric chemistry, standards and legislation (UK and European).

Volume 2: monitoring and control

#### **Package E012**

This package follows on from AE Vol. 1: key issues, and provides detailed information on measurement and monitoring and control techniques, illustrated with comprehensive case studies. Sections on ambient monitoring, meteorology and air dispersion modelling help to provide a thorough grounding in the technical issues associated with air emissions.

### ENERGY MANAGEMENT

#### **Package E011**

Energy efficiency affects the bottom line. Trainees learn the basic tools and techniques for effective energy management.

### ENVIRONMENTAL AUDITING

#### **Package E04**

Trainees learn how to make audits more effective. In clearly defined sections, the package explains how to go about auditing a site, from defining the scope and objectives through on-site activities to reporting and follow-up work. Thirteen case studies and exercises, supported by over 120 slides, include: setting up an EMS; auditing for waste disposal, due diligence and effluence compliance; reporting audit findings; and discussion of photographs of bad practice.

### ENVIRONMENTAL MANAGEMENT SYSTEMS

#### **Package E05**

If you already have an environmental management system, this package will help you gain commitment from your staff. If you are just developing a system, not only will you benefit from the training, but also benchmarking from the detailed case studies will save you time. And if you have still not decided which system to go for (if any), this package will help you make an informed decision.

### ENVIRONMENTAL IMPACT ASSESSMENT

#### **Package E06**

This training package gives you a thorough grounding in the EIA process and techniques. Produced in conjunction with the Institute of Environmental Assessment, the package provides an effective means of training all staff concerned with EIAs.

There are nine case studies provided by leading environmental consultancies. These introduce the practical aspects of the EIA process by examining projects involving a food processing plant, a sewage treatment works, a coastal defence scheme, a pipeline proposal, an oil refinery and a power station.

### WASTE MINIMIZATION

#### **Package E07**

Approaches in the package vary from good housekeeping to complex techniques such as life cycle analysis. This training package shows how to go about it, from defining a strategy through to making sure it happens.

### CONTAMINATED LAND

#### **Package E08**

Trainees learn why contaminated land is important, how and why a company should avoid contamination, and the pros and cons of the key remediation techniques. You will also learn how to use this knowledge to get the most out of the consultants you use.

*For order form contact:*

Mark Smith

Safety Health and Environment Department • Institution of Chemical Engineers  
165-189 Railway Terrace • Rugby CV21 3HQ, UK

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## 4.6 Some background documents on the environment

### **Saving Our Planet: challenges and hopes** [1992]

M.K. Tolba (Executive Director of UNEP).  
ISBN 0 412 47370 4.

This book analyses the changes that have occurred in the environment in the past two decades. It focuses not only on the state of the environment, but also on the interactions between development activities and the environment. It highlights the main responses since 1972 to protect the environment.

*Published by:*

Chapman & Hall, 2-6 Boundary Row,  
London SE1 8HN, UK.

### **Environmental Data Report 1993-1994** [1993]

United Nations Environment Programme.  
ISBN 0 631 19043 0.

This report is updated biennially and provides the best available data and information on a wide range of environmental topics, including pollution, health, natural resources, population and settlements, energy, wastes and disasters.

*Published by:*

Blackwell Publishers, 108 Cowley Road,  
Oxford OX4 1JF, UK.

### **Chemical Pollution: a global overview** [1992]

United Nations Environment Programme.

This book overviews the origins and impacts of pollution around the world, caused by selected chemical pollutants and wastes.

*Published by:*

UNEP, Nairobi.

### **The Earth Summit's Agenda for Change: a plain language version of Agenda 21 and the other Rio Agreements** [1993] M. Keating. ISBN 2 940070 00 8.

This publication is aimed at facilitating access to the very important material contained in Agenda 21.

*Published by:*

The Centre for Our Common Future,  
52 rue des Paquis, 1201 Geneva, Switzerland.

### **Beyond the Limits: global collapse or a sustainable future?** [1992] D.H. Meadows;

D.L. Meadows; J. Randers. ISBN 1 85383 131 X.

Using World 3, a computer model, to project the future, and by varying the basic global policy assumptions, a range of possible outcomes is described. It is shown that a sustainable society is technically and economically feasible, if growth in material consumption and population are ceased and there is an increase in the efficiency of our use of materials and energy.

*Published by:*

Earthscan Publications Ltd.,  
120 Pentonville Road, London N1 9JN, UK.

### **Changing Course: a global business perspective on development and the environment** [1992]

S. Schmidheiny. ISBN 0 262 69153 1.

This book provides an analysis of how the business community can adapt and contribute to the crucial goal of sustainable development, combining the objectives of environmental protection and economic growth.

*Published by:*

Massachusetts Institute of Technology (MIT)  
Press, Cambridge, Massachusetts 02142, USA.

### **Blueprint for Green Management: creating your company's own environmental action plan** [1995]

G. Winter. ISBN 0 07 709015 2.

This book is a handbook of industrial ecology with numerous checklists for practical use and a concrete example of the Integrated System of Environmental Business Management (the so-called Winter Model), supported by the Commission of the European Communities.

*Published by:*

McGraw-Hill Book Company (UK) Ltd.

### **Life Cycle Assessment: what it is and how to do it** [1996] UNEP IE

This report is in two parts. The first, *Life Cycle Assessment: what it is*, is concerned with the concept of LCA, how it is currently practised and



how it is expected to develop. It also places LCA in the broader perspective of other tools for environmental analysis such as environmental impact assessment, risk analysis and technology assessment.

The second part of the volume, *Life Cycle Assessment: how to use it*, examines the several steps involved in making an LCA in a simplified

but systematic manner. It illustrates the problems involved and the kind of results that can be produced by working through a real LCA that has been used to assess the environmental impact of different low fat spreads.

*Further information:*

UNEP IE, Paris, France.





## *Part 5*

# **Training Material**

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# 5 Training Material

## 5.1 Introduction

**T**his part contains exercises covering various issues in lead-acid battery recycling, divided into preliminary and work exercises. Preliminary exercises may be used to function as homework for participants before attending a workshop or course.

The work exercises in this part require a considerable amount of time and a thorough study of the background readings in advance. Further notes and some model answers are provided to help the trainer facilitate the workshop.

The exercises are not suitable for handing out as they are presented. It is left to trainers to adapt the exercises to their particular needs. The trainer should first try to do the exercise, so that they are

not confronted with unexpected problems or questions from the participants!

Most exercises are based on interactive processes, involving groupwork problem solving. However, the exercises can also be done individually. Trainers are encouraged to adapt the given exercises to suit the target audiences, and to develop additional exercises to extend the learning experience.

Further ideas for activities and uses of the material in this package are given below.

## 5.2 Some ideas for training activities

### 5.2.1 Cleaner Production

**Cleaner Production** is the continuous application of an integrated preventative strategy to processes and products, in order to reduce environmental risks and impacts. The cleaner production approach makes use of many environmental management tools, including the *cleaner production audit*. Based on an overall mass balance of a process or site, identifying raw materials, products, wastes and emissions, and energy use, options are devised to minimize the generation of wastes, emissions and energy, to improve the overall performance of the process/site. The *Audit and Reduction Manual for Industrial Emissions and Wastes*, a joint publication of UNEP IE and UNIDO

explains the process of the cleaner production audit step-by-step.

Students can be asked to carry out a cleaner production audit at a secondary lead smelter, using the above mentioned manual as a guidebook. As a result, the students could identify several options to minimize wastes, emissions and energy use of the secondary lead smelter. These options should result in more efficient and cost effective operations.

This assignment could be a project for a team of students, who can spend about two months on it.

Sources for information on cleaner production options are available from EP3, International Lead and Zinc Organization, and other literature sources mentioned in *Part IV*.

### 5.2.2 A visit to a landfill/lead-acid battery collector

**Many lead-acid batteries** are stored inappropriately. This means that they either end up in ditches or uncontrolled landfills, or they go to a controlled landfill for household waste. A visit may be arranged to investigate the destiny of lead-acid batteries in a landfill. Ask about the fate of lead-acid batteries, once they have been dumped in the landfill. This excursion

can also be used to understand the importance of recycling many other products.

Batteries that are dealt with properly end up at a collector, from where they are transported to a secondary lead smelter. A visit to a lead-acid battery collector would give a good idea of the practice of recycling and would enhance a basic understanding of the environmental and human threats posed by used lead-acid batteries.

### 5.2.3 Breaking a lead-acid battery

**Consider examining** a used lead-acid battery in class. You should be able to get one at a service station. Take the lead-acid battery apart during class. While removing the different constituents from the battery, explain the fate of each of them in the secondary lead smelter. Of

course, the acid should be removed with care, and the wrecked battery should be disposed of appropriately after examination.

*Pay attention to, and demonstrate, safe working procedures.*

### 5.2.4 Other recyclable products

**W**hen considering the broader issues of lead-acid battery recycling, you may want to focus your attention on other products and discuss in a plenary session the different recycling schemes of these products.

If recycling schemes for certain products are not yet in existence, they can be developed, taking the lead-acid battery recycling scheme as an example. Ideas for products to discuss are: waste oils, batteries (dry cells), plastics, electrical appliances, and construction material.

### 5.2.5 Slags

**S**lags from secondary lead-smelters are generally dumped in landfills. However, when the heavy metals in the slags are sufficiently immobilized, they can be used for other purposes, e.g. in road construction. You can

ask the students to gather information on the national regulations on the disposal of slags, and other end uses of slags. Of course, the same can be done for other products from lead-acid battery recycling: ebonite, PVC, and polypropylene.



## 5.3 Some ideas for preliminary exercises

### 5.3.1 Introduction

**B**efore starting a learning activity, you can ask trainees to prepare by giving them some preliminary exercises to do.

You may also want to ask them to read some of the articles from the background reading in *Part III* before attending the learning activity.

Most of these preliminary exercises require the trainee to collect information from a number of sources. In order to give some ideas about where to find information, a list of possible sources is given below. You can give this 'checklist' to the trainees in advance. Ask them to mark the information sources they used for the preliminary exercise.

I N F O R M A T I O N   S O U R C E S   U S E D	
Newspapers	University library
International organisations	Public library
Ministries	Local authorities
CD-ROM	Patent office
Information hotlines	Yellow Pages / phone book
Magazines and journals	Industries
Interviews	Wholesalers
Consumer organisations	(International) databases
Labour unions	Industrial organisations
Chambers of Commerce	Non-governmental organisations
Other:	Service Sector:

### 5.3.2 Preliminary Exercise 1

**M**ake an estimate of the total number of batteries from cars which have to be recycled every year in your country. Go to the library, or seek out other information sources, to find out the number of cars in your country and

the average life of lead-acid batteries. If data is not available, estimate the number of cars by consulting statistical data from relevant agencies (which ones?).

Explain your assumptions.

### 5.3.3 Preliminary Exercise 2

**I**nvestigate how the collection of used lead-acid batteries is organized in your country. Also investigate where lead-acid batteries are collected, how and where they are stored, and where they are recycled.

- Are all batteries recycled in your country, or are they (also) exported to other countries?
- To which countries are they sent, or from which countries do you receive used lead-acid batteries?

- Are lead-acid batteries reused in your country, either by recharging or by cosmetically cleaning?
- If so, how is this organised?  
Inquire whether it is possible to visit some typical sites which are part of the lead-acid battery recycling network, and discuss the issues raised in this preliminary exercise with the manager.

### 5.3.4 Preliminary Exercise 3

**T**his preliminary exercise should be done in preparation for the exercise on the lead-acid battery recycling facility. In order to better understand the hazards and risks associated with lead-acid battery recycling, you are asked to do a literature search on the risks associated with the constituents of lead-acid batteries.

The major components of a lead-acid battery are:

- electrodes (lead)
- electrolyte (sulphuric acid)
- casing (plastic).

The positive electrode (the *cathode*) typically consists of a grid pasted with pure lead dioxide, and the negative electrode (the *anode*) consists of a

grid pasted with metallic lead containing various elemental additives to increase the anode's hardness. The additives used depend on the battery manufacturer. The most commonly used additives are antimony, arsenic, cadmium (although not in Europe), copper, selenium, and tin.

*Table 5.1* indicates the type and proportions of constituents of lead-acid batteries. The additives and their typical concentrations ranges are given in *Table 5.2*. The figures in *Table 5.2* are characteristic for Canada and USA. Cadmium is not used as an additive in Europe, because of the environmental problems which occur during recycling. Cadmium forms toxic volatiles during lead-acid battery smelting.

- 1 Search the library for information about the hazards related to each constituent.
- 2 Which international organizations can provide information about these hazards?
- 3 Find articles which discuss cases of lead-poisoning. Could these cases of lead poisoning in any way be related to the activities of lead-acid battery recycling?

**Table 5.1** Constituents of used lead-acid batteries

Component	Per Cent Weight
Metallic lead	17
Lead sulphate	50
Plastic	5
Acid	24
Residuals *	4
<b>Total</b>	<b>100</b>

\* The category *residuals* refers to ebonite and separators.

**Table 5.2** Chemical additives to lead-acid batteries  
(typically in Canadian and US batteries)

Additive	Concentration (%)
Cadmium	0.1 - 0.14
Antimony	2.5 - 7.5
Arsenic	0.15
Tin	0.1 - 0.5
Copper	0.05



## 5.4 Work exercises

### 5.4.1 Obstacles to a perfect recycling scheme

In many countries, the recycling rate of lead-acid batteries is around 90 per cent. However, despite the fact that recycling networks are well organized in many countries, recycling rates are unlikely to reach 100 per cent.

In this exercise, you will identify why a hundred per cent recycling rate cannot be achieved, and why and where in the lead-acid battery recycling network environmental and health risks arise.

The exercise can be done individually as well as in a group. Ideas for answers are provided by the trainer. Other appropriate solutions may also be identified during a plenary session.

Read the article on *Current Management Practices for Used Lead-Acid Batteries in Canada* before answering the questions in this

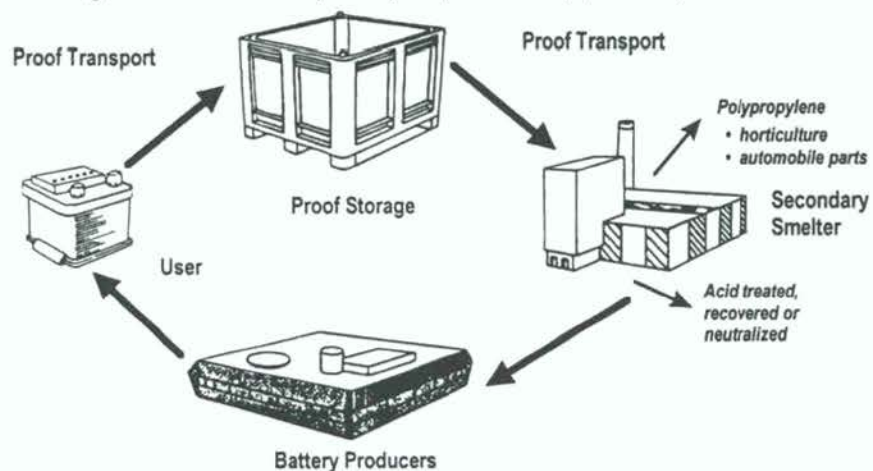
exercise. You will find this article in the background reading in *Part III*.

The article suggests that the lead-acid battery recycling network typically consists of four elements: the consumer, the transportation network, the battery breakers, and the smelting operation.

The relationship between these categories is shown in the first figure in the article. Note that this network is only part of a bigger network for lead-acid batteries in general. This bigger network consists of:

- battery manufacturers
- consumers (car producers/sellers/buyers)
- lead-acid battery collectors (storage) and
- secondary lead-smelters (see *Figure 5.1*).

Figure 5.1 The battery life cycle (*Metaleurop, France*)



All lead-acid batteries have to be collected and recycled in order to minimize the environmental and health risks of inappropriate disposal. Also, all environmental and health risks should be minimized during the collection of lead-acid batteries, and storage of used lead-acid batteries should be avoided as much as possible. As is clear from the background reading in *Part III*, this ideal situation has not been realized by any

country in the world. In some countries, a recycling rate of more than 100% has been achieved, but this is a result of a delay in battery collection in the previous year.

In the following exercise, you are asked to clarify why a yearly recycling percentage for lead-acid batteries of 100% has not been achieved in any country, and what environmental and health risks arise in the lead-acid battery recycling network.





- 1 (a) What constraints are there to prevent the consumer from delivering a lead-acid battery to the retailer, collector, or drop-off depot?

- (b) What environmental threats and health risks occur when the consumer keeps the batteries “in-house” for a long time?

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*Some suggestions for answers to this question are on page V:40*

- 2 (a) Considering the transportation network, what constraints prevent delivery of the batteries to the battery breaker or the secondary lead-smelter?

- (b) What environmental threats and health risks occur when the batteries are stored commercially for a long time?

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*Some suggestions for answers to this question are on page V:40*

- 3 (a) Considering the battery breaker, what constraints are there to prevent delivery of the batteries to the secondary lead-smelter?

- (b) What environmental threats and health risks occur when the battery breaker keeps the batteries for a long time?

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*Some suggestions for answers to this question are on page V:40*

## 5.4.2 Case-study on a lead-acid battery recycling facility

This exercise is based on a case-study describing the recycling process of lead-acid batteries at a recycling facility, and is best done after *Preliminary Exercise 3*.

The participants will – either individually or in a group – do some exercises, which in some cases require a technical background.

The information needed to answer some of the questions in this exercise is provided in the attachments at the end of the exercise.

The results may be discussed in a plenary session, and ideas for answers are again provided at the end of this Part. The trainer should work through the exercises first to become comfortable

with the case-study before asking the participants to do the exercises.

The case-study is based on the article '*A modern and low-pollutant secondary lead smelter to be set up in Hungary*' included in the proceedings of the World Conference on *Hazardous Waste: Detection, Control, Treatment* (See References in *Part IV*).

### Introduction

This exercise concerns a medium sized secondary lead-smelter with an annual capacity of 25 000 tonnes, located near a recreation area. The plant processes used lead-acid batteries and lead scrap. Only the smelting and recycling of the used lead-acid batteries are considered for the purpose of this exercise.

Secondary lead smelting is a highly polluting process, and has been related to many health problems in the past and in the present. The secondary lead smelter described in this exercise was responsible for serious environmental problems in the late 1970s. An unfortunate combination of events culminated in extreme emission rates that poisoned most of the young children playing in the vicinity. The first of these events was related to a change in ownership in 1977 that introduced a new management philosophy to the facility. Smelting capacity was increased by about 35%, and the smelter operators elected to install new production equipment before upgrading pollution control.

In the late 1970s, during a period of extraordinarily high lead prices, an attempt was made to improve air pollution control while the smelter operations continued at the maximum control capacity. The result was a fire that disabled approximately 60% of the smelter's particulate air pollution control capability. However, operations continued with the

remaining equipment, and emissions increased dramatically. Dust conditions within the plant became intolerable, and during the last week of 1979, a decision was made to effectively bypass the main pollution control facility and continue operations.

The bypass continued until April 1980 when repairs were finally completed. Several children were hospitalized, and extensive blood sampling revealed that 95% of all children in the vicinity had blood lead levels in excess of 0.2mg/l (EEC limit, 1977). As a consequence, many residents were relocated, and homes nearest the smelter were purchased and destroyed. Several emission control projects were undertaken. Streets were cleaned and dust producing areas were watered. Home gardening was discouraged. Clean topsoil, sand gravel, grass seedings and water subsidies were provided to promote the general recovery of the community.

Needless to say, these corrective actions were very costly. Additionally, the secondary lead smelter developed a bad public image. Since these accidents, the plant has been committed to meeting stringent environmental restrictions, especially with respect to the following focal points:

- complying with the strict regulations on lead emission;
- providing for optimally clean workplaces.



### Process description

The processes in the plant involve the following three operations:

- 1 **Wrecking** the batteries.
- 2 **Smelting** the prepared batteries and lead slurries by the oxygen process in a short rotary furnace.
- 3 **Refining** the bullion discharged from the short rotary furnace and the scrap lead kettles.

The layout of the plant described above comprises the following sections (see *Figure 5.3* in the attachments).

- wrecking section with storage areas for battery scrap and lead slurries;
- storage bins for fluxes and recycling products and weighing unit for these materials;
- smelting section;
- refining section;
- filtering section.

The batteries collected from scrap yards, wholesalers, and service stations are brought to the facility on Tuesdays. The batteries are stored in an outdoor stockyard from where they are transported to the wrecking section's loader by bulldozer. The stockyard, loader, and crusher are drained during the wrecking phase to collect acid

### Wrecking of the battery scrap

A modern and relatively simple process has been chosen for battery wrecking, involving a minimum of machinery. The process has been exactly tailored to the specified capacity of 1.0 million batteries/year.

The process eliminates operations which – based on modern findings – are superfluous, such as the removal of grid metal and oxide or the removal of separators. The quantity of acid removed by the ventilation system is less than 1% of the total acid content of the batteries, and therefore negligible for the calculation of the mass-balance. However, in order to meet the most stringent health and safety standards, the ventilation system is crucial.

The process involves the following operations:

- **removal of sulphuric acid:** the batteries reach a spike crusher via a vibrating feeder and a chain conveyor. They are perforated to enable

which is then conveyed to the acid tank for further use. The refined lead is stored outside to cool down, after which it is transported to lead manufacturers on Tuesdays and Fridays.

*Table 5.3* indicates the type and proportions of constituents of lead-acid batteries, based primarily on the lead-acid automotive battery.

**Table 5.3** Constituents of used lead-acid batteries

Component	Per Cent Weight
Metallic lead	17
Lead sulphate	50
Plastic	5
Acid	24
Residuals *	4
<b>Total</b>	<b>100</b>

\* The category *residuals* refers to ebonite and separators.

drainage of the acid. The acid is separated on a vibrating screen, and discharged into a settling tank where entrained slurry is allowed to deposit. It is finally stored in a tank for further use. In this phase, 95% of all acid is separated from the batteries.

- **shredding of the batteries and separation of polypropylene** (and of light plastics respectively): the batteries, freed of liquid acid, reach rotary shears. They are cut up and then dropped into a neutralization tank, together with the lead paste. The paste is a mixture of lead oxide and lead sulphates. The solids are discharged from the neutralization tank by means of a screw, and then passed on to intermediate storage. If desired, the floating polypropylene may be discharged separately at this point. The lead paste is collected in the



thickener from where it is discharged to storage for lead fraction.

- **neutralization of the adhering residual sulphuric acid** is carried out in the neutralizing plant, to avoid volatilization of SO<sub>3</sub> inside the furnace. The liquid contained in the tank is transferred by pumping, and neutralized with hydrated lime. The solids content is kept constant by separation of a slurry portion. On average, the ratio of Ca(OH)<sub>2</sub> to sulphuric acid is 1.2:1 on a weight basis.

The polypropylene product is put into the furnace together with the lead-bearing fraction,

and completely burned with the heavy plastics, thus utilizing the calorific value of the latter.

Impacts on the environment resulting from plant operation are avoided by the following measures:

- the chain conveyor for battery transportation is sprinkled with water to avoid dust generation;
- both the spike crusher and the rotary shears are operated at low speed (less than 100 rpm) to counteract the formation of dust and of aerosols;
- accumulating splash water is recycled, which means that no waste water is generated;
- plastics with residual lead content are not dumped.

Now answer the following questions:



- 4 (a) Give three reasons why the sulphuric acid is separated from the lead containing fraction:

- (b) What is the main environmental problem related to SO<sub>3</sub> and SO<sub>2</sub> in the atmosphere?

- (c) In some secondary lead smelters, the lead sulphate in the paste is desulphurized with Na<sub>2</sub>CO<sub>3</sub>. Give the reaction equation, and explain why the lead paste is desulphurized before the smelting process:

*Some suggestions for answers to this question are on page V:40*



- 5 Refer to **Table 5.3**. In this exercise you are asked to calculate a mass balance for the wrecking process for all components of the lead-acid battery.

Assuming an average weight of the lead-acid batteries of 17.2kg, calculate how many kg of metallic lead, lead sulphate/oxide, plastics and residuals per used lead-acid battery are collected at the end of the wrecking operations.

*"Residuals" refers to ebonite and separators (90%), and iron (10%).*

*The answer to this question is on page v:40*

**I**n secondary lead smelters in developing countries, it has often been the case that the batteries are broken manually, without proper protection for workers. This is to allow release of sulphuric acid before smelting (Greenpeace report *Lead Astray: the poisonous lead battery waste trade* [1994]).

For the next question, assume that – in developing countries – the batteries are dumped

in a container at arrival, and from there are transported to a place where the actual breaking of the batteries takes place. The acid is allowed to run off to a settling tank through a gutter, where it is neutralized before being released into a local waterway. The plastic battery cases are cleaned by hand in rinsing baths at the workplace and then stored in a container, which serves as a collector for the feed to the smelter.



- 6 (a) What dangers are the workers exposed to during the battery wrecking operations in developing countries? (See also background material and Materials Safety Data Sheets):

(b) What protective provisions would be necessary to prevent exposure to these hazardous substances? (See also background material and Materials Safety Data Sheets):

*Some suggestions for answers to this question are on page v:40*



### Smelting the correspondingly prepared batteries and lead slurries by the oxygen process in a short rotary furnace

The prepared batteries, along with recycling products from lead refining (drosses), flue dusts, and reagents (soda, CaO, SiO<sub>2</sub>, and Fe-chips), are smelted with oxygen in two short rotary furnaces. During smelting, the antimony, arsenic, tin, calcium, aluminium, and other alloying elements in the grids are oxidized to the slag, while lead is reduced and recovered as a low impurity bullion.

The dust and recycling products from the lead refinery make up 10% of the total weight of the input into the rotary oven, and the reagents added to the smelter make up a further 5%.

The smelting section consists of a feeding device and two short rotary furnaces with 3.5m diameter, equipped with oxy-fuel burners of special design with a capacity of 30–300kg of fuel oil/h and 50–600Nm<sub>3</sub>O<sub>2</sub>/h.

The essential features of smelting with oxy-fuel burners are:

- **reduced fuel oil consumption**, i.e. from approximately 90kg/t of scrap to approximately 40kg/t of scrap;
- **shortened charging period** and, consequently, increase in capacity;
- **reduced generation of dust** and therefore, an increased direct metal recovery (maximum dust content in the cleaned waste gas is 2.5mg/Nm<sub>3</sub>);
- and (an important advantage for environmental protection) **reduction in waste gas volume** from approximately 12m<sup>3</sup>/kg of fuel oil when using air for combustion to approximately 3.2m<sup>3</sup>/kg of fuel oil when using oxygen. This reduction of waste air, in combination with a lower lead content of the flue dusts (from 50% to 35%), minimises lead emission.

The temperature of the waste air is about 1200°C when leaving the furnace, and it has to be rapidly cooled down to below 300°C to avoid formation of dioxins. Dust from the waste air handling system is caught in a combination of electric precipitators, bag filters and scrubbers. The dust is then discharged into the short rotary furnace.

Until now, the use of oxygen in a short rotary furnace was limited to the smelting of metal and lead paste after removal of the plastic components. The modern oxygen process applied

in this particular case enables the smelting of battery scrap including the complete plastic material. This plastic portion is burned smoke-free with full utilization of its heat content. To achieve this, the crushed batteries are charged into the furnace with the aid of a vibrating feeder (see *Figure 5.5* in the attachments) more slowly than usual. During this feeding operation, the furnace revolves slowly, either continuously or intermittently, with the burner ignited.

During combustion of plastics, the fuel oil feed rate is decreased, but the oxygen feed rate is increased.

Such retarded feeding and immediate ignition and combustion of the plastic material avoids not only an uncontrolled, sudden evaporation of the volatiles contained in the plastic material, but also incomplete combustion. These phenomena can hardly be prevented if the furnace, fully charged with plastic-containing batteries, is ignited and turned.

The ratio between material and oxygen feed rate and, consequently, the plastics combustion capacity of the furnace, can be controlled in such a manner that the plastics are burned unhindered and smoke-free. As soon as charging of the furnace and combustion of the plastics have finished, the fuel oil feed rate is increased and the batch is processed.

In the short rotary furnace, both oxidizing and reducing conditions are produced simultaneously. The antimony, arsenic, tin, calcium, aluminium, and other alloying elements in the grids and straps is oxidized to the slag while lead is reduced and recovered as a low impurity bullion. The slag composition is shown in *Table 5.4*.

**Table 5.4** Slag composition in per cent weight

PbO	20 - 30
Sb <sub>2</sub> O <sub>3</sub>	4 - 8
SnO <sub>2</sub>	0.5 - 2
As <sub>2</sub> O <sub>3</sub>	0.5 - 1
CaO	4 - 10
SiO <sub>2</sub>	7 - 17



For meeting the requirements on clean workplaces, it was stipulated from the beginning of the project that feeding and tapping are carried out with the suction system continuously operating. For that reason, both ends of the short rotary furnaces have been equipped with hoods. These hoods (at both the tapping and the feeding end) have been designed in such a manner that they offer enough space to accommodate the

number of ladles needed for one lead and/or slag tapping operation. The ladles are kept under the hood with the suction system permanently operating until the melt surface has solidified and smokeless transportation is possible. The charge is taken to a vibrating feeder with the aid of an enclosed chain conveyor. The feeder has also been integrated in the hood, thus completely avoiding dust formation during furnace feeding.

Now answer the following questions.



- 7 Due to the use of oxy-fuel burners, the generation of lead in dust has decreased considerably. Exactly how much has lead in dust been reduced, per tonne of battery scrap?

*The answer to this question is on page V:41*

- 8 Calculate the fractions of the constituents and the total weight of each load in the two short rotary furnaces, based on an annual capacity of the facility of 1 million used lead-acid batteries. Assume the furnaces are in operation for five days a week, 42 weeks a year. The furnaces are charged five times per day:

*The answer to this question is on page V:41*

Due to new environmental regulations which will be enforced in the near future, the recycling plant will have to separate all components of the batteries. Therefore, the wrecking process has to be changed.



**9 Design the new process flow-diagram of the wrecking process.**

Make a process-flow diagram, using boxes to illustrate the separation process, and arrows to indicate the direction of the flow of the materials. Separation techniques based on size distribution and hydrodynamic characteristics will suffice for separating all end products. The end products are: grids, lead paste, PVC/ebonite, acid, and polypropylene. Use water for the different separation phases and neutralization phases:

*A suggested answer to this question is on page V:41*

**10** Due to the separation phase, polypropylene and acid can be processed and sold as raw materials.

*(a)* Do you expect that the capacity of the smelters will change due to the new separation process?

*(b)* How will the energy consumption per tonne of lead change?

*Answers to this question are on page V:41*

## Refining of bullion discharged from the furnace and of scrap lead

**R**efining of bullion is carried out by a standard process (kettle refining) in five kettles of 50t capacity each. Refining will include the following operations:

- smelting and drossing;
- copper removal;
- softening (antimony removal);
- final clean-up, alloying and casting.

Lead refining is known to have environmental impacts and to be hazardous to the health of workers. The removal of reaction and intermediate products from the kettle is particularly dangerous because it often involves significant danger for the personnel due to the occurrence of lead-bearing dusts and high temperatures.

To eliminate these dangers and for meeting the requirements of national labour regulations, the following technical appliances are provided:

- hoods for the kettles enabling an automatic adjustment of the waste-air volume;
- mechanical removal of drosses and transfer of these into closed containers;
- pneumatic transportation of the drosses from the containers into the bins;
- transportation of the drosses from the bins to the short rotary furnace in enclosed conveying units.

The above description shows that all process operations, including transportation, are performed in closed containers without any

intermediate product being handled and transported uncovered.

The hoods (see *Figure 5.6* in the attachments) have been designed in such a way that the elements (i.e. an agitator, a pump, or an agitator joined to a withdrawing unit) can be integrated into the hood. The quantity of sucked-off waste air is automatically adjusted to the minimum volume required for each operation, thus minimizing the overall quantity of waste air discharged from the refining plant.

The drosses are removed with the aid of a screw conveyor. Previously, the drosses were removed manually, causing a serious deterioration in working conditions. The screw conveyor can be vertically adjusted for varying the immersion depth into the fluid layer. The fluid layer is moved by an agitator towards the inlet opening of the screw conveyor, lifted beyond the kettle rim by the spiral grooves of the screw, and continuously transferred into a closed container. After dross removal is complete, the container content is allowed to cool down. The cooled content is sucked off with a suitable device and pneumatically delivered into a bin.

The method explained above permits removal of the fluid reaction products from the melt surface and transportation to the bin section without involving any danger for the operating staff.

## Conclusions

**T**he plant described above has been designed to produce approximately 60% of quality 99.95% purity and the balance of approximately 40% of hard lead, based on the intended annual quantity of feed material of one million lead-acid batteries. An overall recovery of 97.2% will be obtained. Any intermediate product accumulating in the plant, such as flue dusts and drosses, are recycled. This is also true of service- and process water. Chlorine, if any, originating from PVC is precipitated with lead flue dust and transformed into a rotary furnace slag in special flue dust campaigns.

Two end products are discharged from the plant: *market lead* and *slag*, originating from the short rotary furnace which is taken to a dump. This slag is the only loss and waste product accumulating in the plant.

Apart from the measures described above, several other technical and organizational actions have been implemented for ensuring as clean a workplace as possible. The most important of these additional measures are:

- All walls and ceilings of any plant section are smooth on the inside;



- Sprinkling systems for walls are installed to permit cyclic washing;
- Floors and platforms are inclined towards the drain and the channel: water spray nozzles are installed at elevated points for cyclic sprinkling of the surfaces;
- Essential plant areas have been laid out in such a manner that no vehicles are required, thus eliminating the entrainment of dust deposits;
- Control stands and short-break rooms, as they are called, have been built: these are only

accessible via gates, and are supplied with air from outside over high-duty filters.

Processing of battery scrap and lead residues is certainly a difficult problem to cope with because of toxicity of the lead and complicated handling operations. The plant design described above shows that the application of modern technologies and improved working conditions to standard technologies permit the erection of a plant at reasonable expenditure which meets current job and environmental regulations.

Now answer the following questions.



- 11 (a) What environmental threats does the secondary lead smelter pose to its vicinity? Discuss, for each stage of the process, the operations and substances which may cause environmental pollution during normal operations:

- (b) What about when there is a malfunction/accident in the facility (e.g. fire, collision, open valves, etc.)?

*Suggested answers to this question are on page V:41*

- 12 (a) For what purposes could the slags be used, instead of being dumped at a landfill?

- (b) What environmental problems can slags cause when used for these purposes, taking into account the origin and contents of the slags?

*Suggested answers to this question are on page V:42*



- 13 During the smelting and refining process and the recycling of dust, a lot of energy is used and wasted as heat. Where in the total process could you reuse the heat lost during smelting, refining and cooling, in order to save energy during the smelting and refining process?

*Ideas for answering this question are on page V:42*

- 14 According to the World Bank report on *Occupational Health and Safety Guidelines*, exposure to employees should never exceed  $50\text{mg}/\text{m}^3$ . The plant described above fulfils these norms, thanks to the hood structure above the furnaces. Before the hood structure was installed, a ventilation system removed the lead particles from the hall.

Assume that the hall where the two short rotary furnaces are located has a volume of  $3600\text{m}^3$ . When in operation, the two short rotary furnaces together emit  $60\text{g}/\text{h}$  of lead in particle form per  $1\text{m}^3$ , due to leaks. How many cubic metres must the ventilation system be able to clear of lead per hour in order to keep the lead particle concentration below the limit?

*A suggested answer to this question is on page V:42*



---

15 Fugitive emissions arise during various batch and transfer operations. In addition, waste treatment procedures also play a significant role. Accordingly, emissions from a process can vary considerably, depending on the degree of 'good housekeeping practice', supervision and control exercised at a plant.

Give suggestions on how to reduce human exposure to lead through 'good housekeeping practices':

---

*Suggestions for answers to this question are on page V:43*

---

16 How should the design of the batteries be changed in order to reduce the environmental impacts during the recycling process? Keep in mind that the performance of the battery must not be reduced:

---

*Suggestions for answers to this question are on page V:43*

---

17 Based on the lead recuperation rate at the refinery, how many batteries can be produced only using lead which is produced by this secondary lead smelter? Assume that new batteries contain 10kg of lead.

---

*Suggestions for answers to this question are on page V:43*



## 5.4.3 Attachments to the case study

Figure 5.2 Model for air emission inventories and controls

PROCESS	UNIT (U)	TSP kg/U	SO <sub>2</sub> kg/U	NO <sub>x</sub> kg/U	CO kg/U	VOC kg/U		kg/U
Fabric filter	tn of Pb	0.07						
<b>SECONDARY LEAD PROCESSING</b>								
<b>Pretreatment</b>								
Sweating furnace								
Fugitive emissions	tn of Pb	1.3					Pb	0.55
Uncontrolled	tn of Pb	25.5					Pb	6
Controlled	tn of Pb	0.25					Pb	0.06
<b>Smelting</b>								
Fugitive emissions	tn of Pb	8.2					Pb	2.19
Reverberatory Furnace								
Uncontrolled	tn of Pb	162	40				Pb	32
Controlled	tn of Pb	0.5	40				Pb	0.1
Blast (cupola)								
Uncontrolled	tn of Pb	153	27				Pb	52
Controlled	tn of Pb	1.12	27				Pb	0.15
<b>Refining</b>								
Kettle refining								
Uncontrolled	tn of Pb	0.02					Pb	0.006
Controlled	tn of Pb							
Kettle oxidation								
Fabric filter	tn of PbO	>20.0					PbO	>20.0
<b>STORAGE BATTERY PRODUCTION</b>								
Uncontrolled *	1000 batteries	63.2					Pb	6.94
Controlled	1000 batteries	3.2					Pb	0.5
<b>PRIMARY ZINC SMELTING Pyrometallurgical process</b>								
Fugitive emissions	tn of zinc	3.85						
<b>Roasting</b>								
Multiple hearth roaster								
Uncontrolled	tn of zinc	113	1100					
Cyclone + ESP	tn of zinc	0.5	1100					
H <sub>2</sub> SO <sub>4</sub> plant	tn of zinc	0.34	33					
Suspension roaster								
Uncontrolled	tn of zinc	1000	1100					
Cyclone + ESP	tn of zinc	4	1100					
H <sub>2</sub> SO <sub>4</sub> plant	tn of zinc	3	33					
Fluidized bed roaster								
Uncontrolled	tn of zinc	1083	1100					
Cyclone + ESP	tn of zinc	4	1100					
H <sub>2</sub> SO <sub>4</sub> plant	tn of zinc	3.2	33					
<b>Sinter plant</b>								
Uncontrolled	tn of zinc	62.5	110					
Cyclone	tn of zinc	24.1	110					
Cyclone + ESP	tn of zinc	8.25	110					

\* A fabric filter is considered an integral part of the lead oxide mill, if any.

Figure 5.3 Overall plant layout

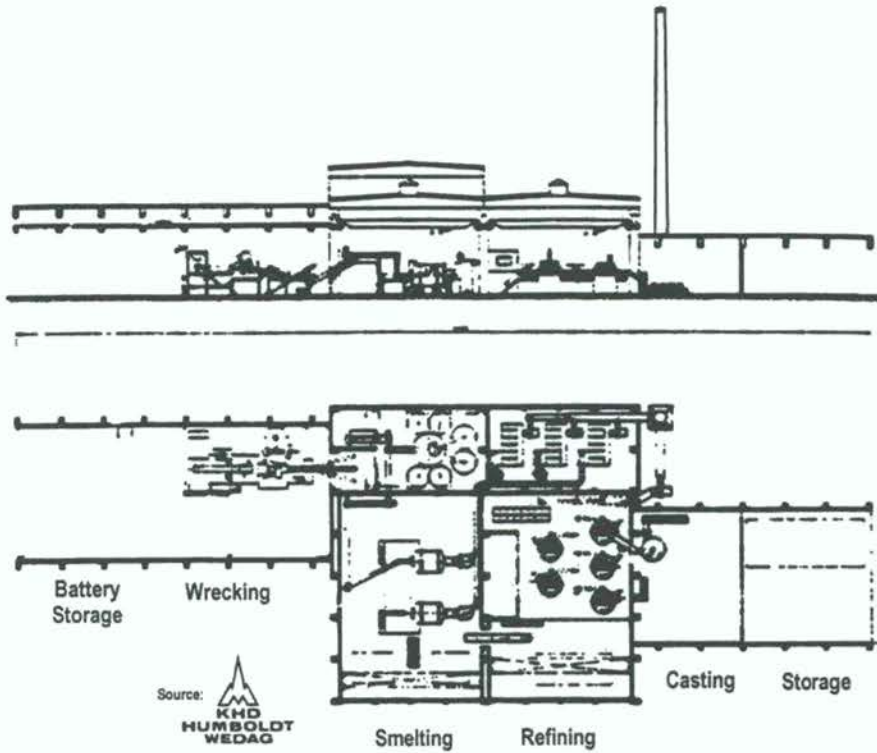


Figure 5.4 Wrecking section

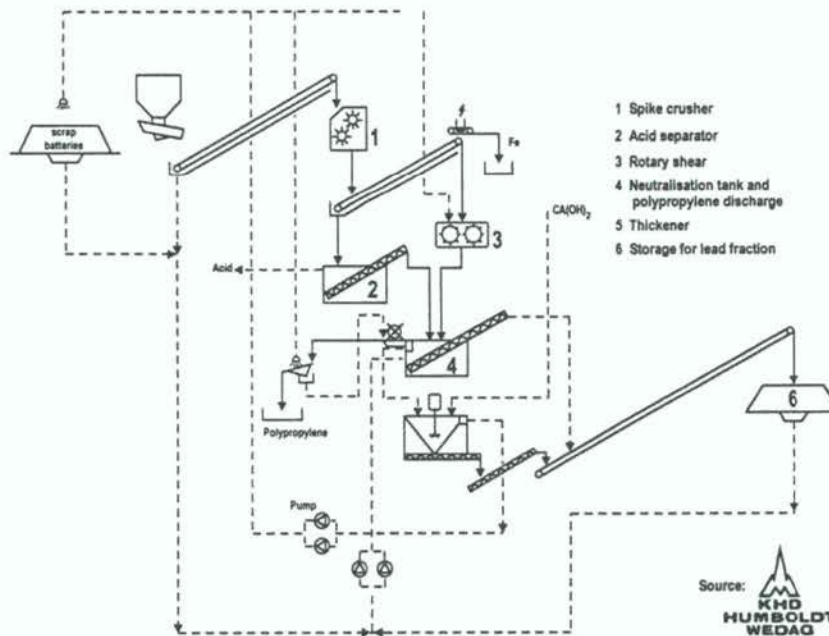


Figure 5.5 Short rotary furnace with hood

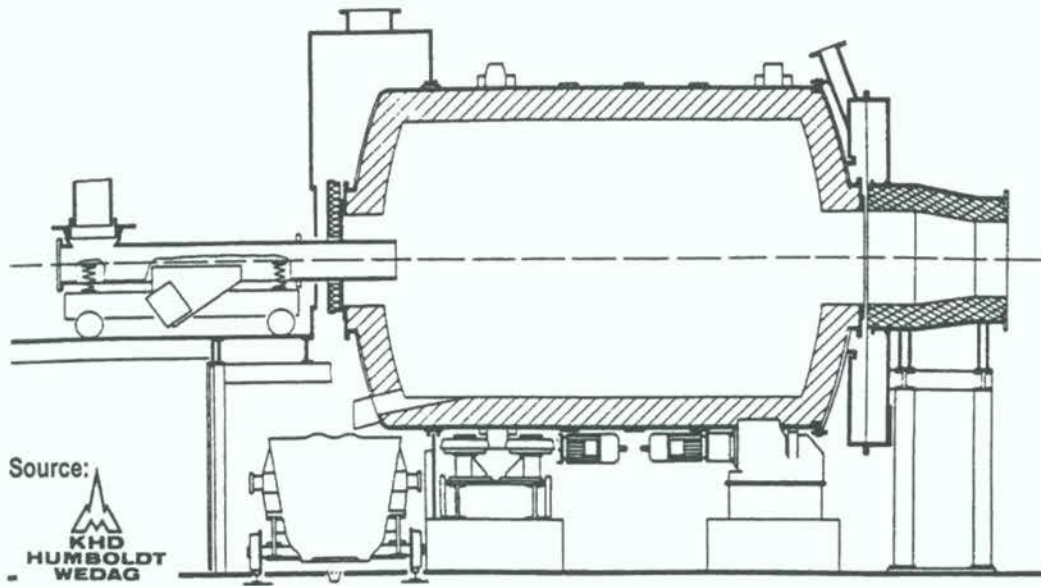


Figure 5.6 Kettle with hood, agitator and removing screw

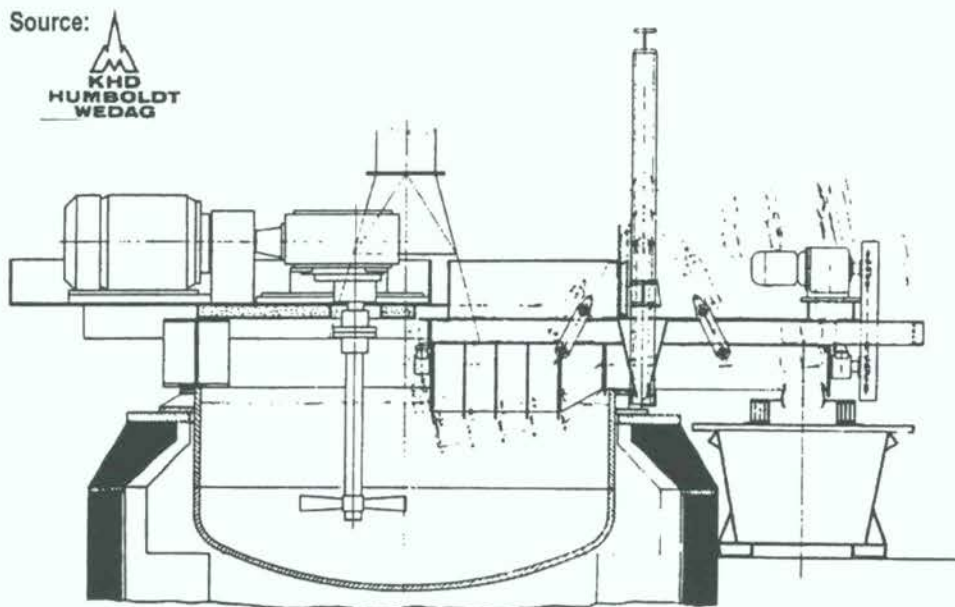




Figure 5.7 Material Safety Data Sheet for lead (inorganic)

<b>Lead (inorganic)</b>		<b>ICSC: 0052</b>	
CAS# 7439-92-1	Lead metal		
RTECS# OF7525000	Plumbum		
ICSC# 0052	Pb		
Atomic mass: 207.2			
<hr/>			
Types of Hazard/Exposure	Acute Hazards/Symptoms	Prevention	First aid/Fire fighting
FIRE	Not combustible		
EXPLOSION			
<hr/>			
EXPOSURE		<i>Prevent dispersion of dust! Strict hygiene!</i>	
• Inhalation	Headache, nausea, abdominal spasm.	Local exhaust or breathing protection	Fresh air, rest, and refer for medical attention
• Skin			
• Eyes			
• Ingestion	Headache, nausea, sore throat, abdominal spasm.	Do not eat, drink, or smoke during work.	Rinse mouth , induce vomiting ( <i>only in conscious persons!</i> ) and refer for medical attention
<hr/>			
Spillage Disposal	Storage	Packaging and Labelling	
Sweep spilled substance into containers, carefully collect remainder (extra personal protection P2 filter respirator for harmful particles).			
<hr/>			
Additional Information			
<b>SEE IMPORTANT INFORMATION ON BACK</b>			
ICSC: 0052      V1.0		Prepared in the context of cooperation between the	
IMPORTANT LEGAL NOTICE ON BACK		IPCS and the Commission of the European	
		Communities © CEC, IPCS, 1990	

continued ...



Figure 5.8 Material Safety Data Sheet for lead (II) oxide

<b>Lead (II) Oxide</b>		<b>ICSC: 0288</b>	
CAS# 1317-36-8	Lead monoxide	<b>HAZARD SYMBOL</b>	
ICSC# 0288	PbO	<i>Consult national legislation</i>	
EC# 082-001-00-6	Molecular mass: 223.2		
<b>Types of Hazard/Exposure</b>			
<b>Acute Hazards/Symptoms</b>	<b>Prevention</b>	<b>First aid/Fire fighting</b>	
FIRE	Not combustible	In case of fire in the surroundings, all extinguishing agents allowed.	
EXPLOSION			
<b>EXPOSURE</b>			
<i>Prevent dispersion of dust. Strict hygiene. Avoid exposure of pregnant women. Avoid exposure of adolescents and children</i>			
• Inhalation	Cough, headache, nausea.	Local exhaust or breathing protection	Fresh air, rest, and refer for medical attention
• Skin	Redness.	Protective gloves.	Remove contaminated clothes, rinse skin with plenty of water or shower.
• Eyes	Redness, pain.	Safety goggles.	First rinse with plenty of water for several minutes (remove contact lenses if easily possible) then take to a doctor.
• Ingestion	Abdominal cramps, constipation, diarrhoea, headache, nausea, vomiting.	Do not eat, drink, or smoke during work.	Rinse mouth, give nothing to drink, and refer for medical attention
<b>Spillage Disposal</b>		<b>Storage</b>	<b>Packaging and Labelling</b>
Sweep spilled substance into containers, carefully collect remainder (extra personal protection P2 filter respirator for harmful particles).		Separated from sodium, aluminium.	<b>Further information on labelling:</b> <i>Consult national legislation.</i>
<b>Additional Information</b>			
<b>SEE IMPORTANT INFORMATION ON BACK</b>			
ICSC: 0288	V1.0	Prepared in the context of cooperation between the IPCS and the Commission of the European Communities © CEC, IPCS, 1991	
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*continued ...*





Figure 5.9 Material Safety Data Sheet for sulphuric acid

<b>Sulphuric Acid</b>		<b>ICSC: 0362</b>	
CAS# 7664-93-9	Sulphuric acid	<b>HAZARD SYMBOL</b>	
RTECS# WS5600000	H <sub>2</sub> SO <sub>4</sub>	<i>Consult national legislation</i>	
ICSC# 0288	Molecular mass: 98.1		
UN# 1830			
EC# 082-001-00-6			
Types of Hazard/Exposure	Acute Hazards/Symptoms	Prevention	First aid/Fire fighting
<b>FIRE</b>	Not combustible. Many reactions may cause fire or explosion.	No contact with flammable substances.	No water.
<b>EXPLOSION</b>			In cases of fire, keep drums etc. cool by spraying with water but <b>no</b> direct contact with water.
EXPOSURE	<i>Avoid all contact!</i>		
• Inhalation	Sore throat, cough, laboured breathing.	Ventilation, local exhaust, or breathing protection.	Fresh air, rest, half-upright position, artificial respiration if indicated, and refer for medical attention.
• Skin	Pain, serious skin burns.	Protective gloves, protective clothing.	Remove contaminated clothes, rinse skin with plenty of water or shower, and refer for medical attention.
• Eyes	Pain, severe deep burns.	Face shield or eye protection in combination with breathing protection.	First rinse with plenty of water for several minutes (remove contact lenses if easily possible) then take to a doctor.
• Ingestion	Severe pain, vomiting, shock.	Do not eat, drink, or smoke during work.	Rinse mouth, give plenty of water to drink, do <b>not</b> induce vomiting, and refer for medical attention.
Spillage Disposal	Storage	Packaging and Labelling	
Evacuate danger area, collect leaking liquid in sealable containers (extra personal protection: complete protective clothing including self-contained breathing apparatus).	Separated from other materials (see Notes), store in stainless steel containers.	Unbreakable packing: put breakable packaging into closed unbreakable container. <b>Further information on labelling:</b> <i>Consult national legislation.</i>	
Additional Information			
SEE IMPORTANT INFORMATION ON BACK			
ICSC: 0362	V1.0	Prepared in the context of cooperation between the	
<b>IMPORTANT LEGAL NOTICE ON BACK</b>		IPCS and the Commission of the European	
		Communities © CEC, IPCS, 1991	

*continued ...*



<b>Important data</b>	<p><b>Physical State Appearance:</b> Colourless, oily, hygroscopic liquid with no odour.</p> <p><b>Chemical Dangers:</b> On combustion, forms toxic fumes (sulphur oxides). Upon heating, toxic fumes are formed. The substance is a strong oxidant and reacts violently with combustible and reducing materials. The substance is a strong acid – it reacts violently with bases and is corrosive to most common metals, forming a flammable gas (hydrogen: see ICSC#0001). Reacts violently with water and organic materials with evolution of heat.</p> <p><b>Occupational Exposure Limits:</b> TLV 1mg/m<sup>3</sup> (as TWA), 3mg/m<sup>3</sup> (as STEL) (ACGIH 1988–1989).</p> <p><b>Routes of Exposure:</b> The substance can be absorbed into the body by inhalation of its aerosol and by ingestion.</p>	<p><b>Inhalation Risk:</b> Evaporation at 20°C is negligible: a harmful concentration of airborne particles can, however, be reached quickly by spraying.</p> <p><b>Effects of Short Term Exposure:</b> The substance is very corrosive to the eyes, the skin and the respiratory tract. Corrosive on ingestion as well. Inhalation of an aerosol of this substance may cause lung oedema (see Notes).</p> <p><b>Effects of Long-Term or Repeated Exposure:</b> Lungs may be affected by repeated or prolonged exposure to an aerosol of this substance. Risk of tooth erosion upon repeated or prolonged exposure to an aerosol of this substance.</p>
<b>Physical properties</b>	<p>Boiling point (decomposes) ..... 340°C  Melting point..... 10°C  Relative density (water = 1) ..... 1.8  Solubility in water ..... miscible  Vapour pressure Pa at 146°C..... 0.13  Relative vapour density (air = 1) ..... 3.4</p>	
<b>Environmental data</b>	Possible harmful effects to aquatic life due to acidity.	
<b>Notes</b>	<p>The symptoms of lung oedema often do not become manifest until a few hours have passed and they are aggravated by physical effort. Rest and medical observation is therefore essential. Never pour water into this substance: when dissolving or diluting, always add it slowly to the water. Store in an area having corrosion resistant concrete floor.</p> <p>Transport Emergency Card: TEC(R) – 10b  NFPA Code: H3, F0, R2, W</p>	
<b>Additional information</b>		
<p>ICSC: 0362 © CEC, IPCS, 1991 Sulphuric acid</p>		
<p>LEGAL NOTICE Neither the CEC nor the IPCS nor any person acting on behalf of the CEC or the IPCS is responsible for the use which might be made of this information.</p> <p>This card contains the collective views of the IPCS Peer Review Committee and may not reflect in all cases all the detailed requirements included in national legislation on the subject.</p> <p>The user should verify compliance of the cards with the relevant legislation in the country of use.</p>		



#### 5.4.4 Life cycle of lead-acid batteries and lead

**I**n this exercise, you are asked to draw the life cycle of lead-acid batteries and of lead. The purpose of the exercise is to understand the differences between a *product life cycle* and a *material life cycle*.

Depending on the amount of time available, you may want to ask broader questions, such as what mining activities are involved, how big is the waste stream involved, how many products are made of lead, how much energy is used for lead-acid battery production, how much pollution does this involve, how much lead is recycled and how, etc. This may require considerable literature study, so the trainer may want to collect some data and background material in advance. Some useful background material is attached. UNEP IE's *Industry and Environment* Nos. 2 and 3 of 1994 focus on recycling. You may find these issues useful for this exercise.

The exercise is best done in small groups (2-4 persons), with half of the groups developing the life cycle of lead-acid batteries, and the other half the life cycle of lead. The trainer will have to give continuous assistance as to how detailed the life cycle should be.

To facilitate the exercise, it is advisable to use either blackboard or a flipchart for drawing the life cycles.

A recent UNEP publication on *Life Cycle Assessment* would make useful preliminary reading, and give further ideas for exercises and projects.

#### INTRODUCTION

**R**ecycling plays an important role in the concept of sustainable development, and especially the recycling of non-renewable resources. This becomes clear when looking at the definition of sustainable development: *a development that meets the needs of the present generations without compromising the ability of future generations to meet their own needs*.

Recycling of materials and products aims to reduce the environmental impacts of these materials and goods, and to reuse resources.

If we don't recycle lead but let it disperse in the environment, this resource will eventually be exhausted.

There are two approaches when looking at recycling. You can look at the recycling of a

*product*, focusing on all constituents of the product, or you can look at the recycling of a *raw material*, focusing on all its applications.

When talking about recycling lead, you need to look at all the stages of the life cycle of lead: from mining through refining, up to manufacture, consumption and disposal of the products in which lead is used.

When talking about recycling lead-acid batteries, you need to look at all stages of the life cycle of lead-acid batteries. That means you start at the excavation and production of its constituents: lead, sulphuric acid, PVC, antimony, tin, etc., and you finish with the recycling and/or disposal of the different components of the lead-acid battery.

## ASSIGNMENTS

Read the background paper below, on *Analytical tools for identifying Cleaner Production opportunities*. This paper is taken from the United Nations Industrial Development Organization (UNIDO) Training Course: *Ecologically Sustainable Industrial Development*.

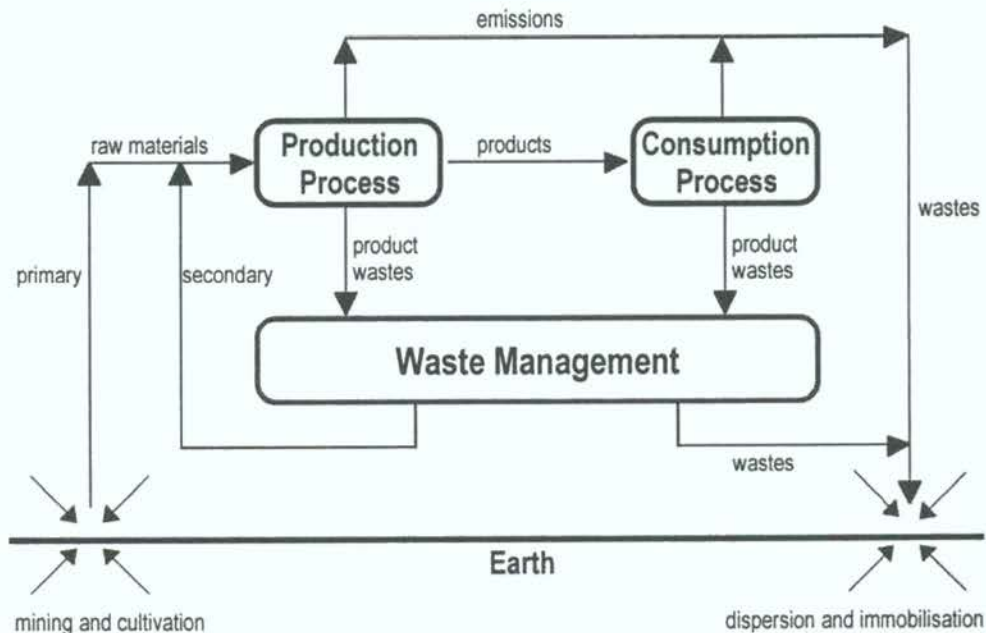
Divide the participants in two groups (depending on the number of participants you can divide the participants into groups of 2, 4, or 8).

**Group 1** Ensure that every phase from production or extraction of PVCs (and its raw materials), lead, sulphuric acid (and their raw materials), polypropylene (and its raw materials), and the production of the other constituents is visible in the drawing.

**Group 2** Design the life cycle of lead. Ensure that every phase, from mining to disposal, is visible in the drawing. Name the different products in which lead is used, but don't describe the other resources needed to make the product, e.g. when describing the use of lead in gasoline, don't include oil refining in the drawing. Remember that lead is also used as a component of other chemical substances, e.g. in pesticides, or its oxides.

Use the background materials in the attachments and those provided by the trainer to understand the life cycle, and use the data in these documents to design your life cycle of lead. Use **Figure 5.10** as an example of how a drawing of the life cycle could look.

Figure 5.10 The life cycle





After drawing the life cycle, prepare a presentation, explaining the life cycle of the chosen subject. After the presentation, a plenary discussion could be initiated, raising some of the following questions:

- What information is missing from the drawn life cycle in order to be able to decide whether recycling of lead/lead-acid batteries is beneficial for the environment?
- How can life cycle analysis be useful for deciding on the benefits of recycling a product?
- How can or should 'environmental costs' be incorporated in calculating the true costs of a product?

### Recommended literature

*Life Cycle Assessment: what it is and how to do it* [1996] Paris, France: United Nations Environment Programme, Industry and Environment Centre.

*Environmental Aspects of Selected Non-ferrous Metals (Cu, Ni, Pb, Zn, Au) Ore Mining: A Technical Guide* [1991] Technical Report Series No. 5. Paris, France: United Nations Environment Programme, Industry and Environment Centre.

*IARC Monographs on the evaluation of the carcinogenic risk of chemicals to humans: Some Metallic Compounds* [1980] Volume 23.

Geneva: World Health Organization, International Agency for Research on Cancer.  
**IRPTC Data Profile on: Lead** [1990] Geneva: International Registration of Potentially Toxic Chemicals, United Nations Environment Programme (IRPTC/UNEP).

**Risk Reduction Monograph No. 1: Lead Background and National Experience with Reducing Risk** [1993] Paris: Organization for Economic Co-operation and Development, Environment Directorate.

**World Directory: Secondary Lead Plants** [1994] Fifth edition. London: International Zinc and Lead Study Group.

### Attachments to the Exercise on the Life Cycle of Lead-Acid Batteries and Lead

#### Analytical tools for identifying Cleaner Production opportunities: Reading Excerpts

##### Identifying and setting boundaries for life-cycle stages

**T**he quality of a life-cycle inventory depends on an accurate description of the system to be analyzed. The necessary data collection and interpretation is contingent on proper understanding of where each stage of a life cycle begins and ends.

##### General scope of each stage

###### **Raw materials acquisition**

This stage of the life cycle of a product includes the removal of raw materials and energy sources from the earth, such as the harvesting of trees or the extraction of crude oil. Transport of the raw materials from the point of acquisition to the point of raw materials processing is also considered part of this stage.

###### **Manufacturing**

The manufacturing stage produces the product or package from the raw materials and delivers it to consumers. Three substages or steps are involved in this transformation: materials manufacture, product fabrication, and filling/packaging/distribution.



**Materials manufacture:** This step involves converting raw material into a form that can be used to fabricate a finished product. For example, several manufacturing activities are required to produce a polyethylene resin from crude oil. The crude oil must be refined; ethylene must be produced in an olefins plant and then polymerized to produce polyethylene; transportation between manufacturing activities and to the point of product fabrication is considered part of materials manufacture.

**Product fabrication:** This step involves processing the manufactured material to create a product ready to be filled or packaged; for example, blow moulding a bottle, forming an aluminium can, or producing a cloth diaper.

**Filling/packing/distribution:** This step includes all manufacturing processes and transportation required to fill, package, and distribute a finished product. Energy and environmental wastes caused by transporting the product to retail outlets or to the consumer are accounted for in this step of a product's life cycle.

#### Issues that apply to all stages

The following general issues apply across all four life-cycle stages:

##### **Energy and transportation**

Process and transportation energy requirements are determined for each stage of a product's life cycle. Some products are made from raw materials such as crude oil, which are also used as sources of fuel.

Use of these raw materials as inputs to products represents a decision to forego their fuel value. The energy value of such raw materials that are incorporated into products typically is included as part of the energy requirements in an inventory analysis. Energy required to acquire and process the fuels burned for process and transportation use is also included.

##### **Environmental waste aspects**

Three categories of environmental wastes are generated from each stage of a product's life cycle: atmospheric emissions, water-borne wastes, and solid wastes.

These environmental wastes are generated by both the actual manufacturing processes and the

#### **Use/reuse/maintenance**

This is the stage consumers are most familiar with: the actual use, reuse and maintenance of the product. Energy requirements and environmental wastes associated with product storage and consumption are included in this stage.

##### **Stages of a life cycle**

- Raw materials acquisition
- Manufacturing
  - materials manufacture
  - product fabrication
  - filling/packaging/distribution
- Use/reuse/maintenance
- Recycle/waste management

#### **Recycle/waste management**

Energy requirements and environmental wastes associated with product disposition are included in this stage, as well as post-consumer waste management options such as recycling, composting, and incineration.

use of fuels in transport vehicles or process operations.

##### **Waste management practices**

Depending on the nature of the product, a variety of waste management alternatives may be considered: landfilling, incineration, recycling, and composting.

##### **Allocation of waste or energy among primary and co-products**

Some processes in a product's life cycle may produce more than one product. In this event, all energy and resources entering a particular process and all wastes resulting from it are allocated among the product and co-products. Allocation is most commonly based on the mass ratios of the products, but there are exceptions to this.

##### **Summing the results of each stage**

To calculate the total results for the entire life cycle of a particular product, the energy requirements and certain emission values for each stage of the product's life cycle can be summed. For example, energy requirements for each stage are converted from fuel units to million British

Thermal Units (BTUs) or megajoules and summed to find the total energy requirements.

Solid wastes may be summed in pounds or converted to volume and summed. The current, preferred practice is to present the individual environmental releases into each of the environmental media on a pollutant-by-pollutant basis. Where such specificity in an external study would reveal confidential business information, exceptions should be made on a case-by-case

basis. Claims for confidentiality should be made only when it is reasonable to expect that release of the information would damage the supplier's competitive position. Even then, the data inputs to an external use are legitimately expected to be independently verified.

A peer review process leading to agreed-upon reporting is one possible mechanism for dealing with this issue. Other approaches for independent verification are possible.

**Table 5.5** Recyclable/non-recyclable applications for lead

Recyclable	Non-recyclable
Batteries	Gasoline additives
Roofing/flashings	Glass
Pipes	Plastics stabilizers
Cable sheaths	Shot-ammunition
Radiation shielding	Paint pigments
Window frames	Solders
Yacht keels	Ceramic glazes
Wheel weights	

**Table 5.6** Recovery of lead products

Product	Product Recovery (%)	Life Cycle (years)
Batteries:		
<i>automobile</i>	~90	3-4
<i>traction</i>	~100	4-6
<i>stationary</i>	~100	up to 10
Sheet	90-95	50-100
Pipe	70-80	50-100
Cable sheathing	50	40

Table 5.7 Battery recycling rates in some OECD countries

	1986	1987	1988	1989	1990	1991
<i>Australia</i>						90
<i>Belgium</i>	77					
<i>Canada</i>						93
<i>France</i>	80			90		
<i>Germany FR</i>	83					>95
<i>Italy</i>	83					
<i>Japan</i>	92.3	92.5	95.2	93.8	92.2	
<i>Spain</i>	83					
<i>Sweden</i>						>100e
<i>United Kingdom</i>	84					93
<i>United States</i>		88.6	91.0	95.3	97.7	

*e = estimated.*

*Note:* Methods used to determine rates may vary by country. Recycling rates can exceed 100 per cent when stored or stockpiled batteries are returned.

*Sources:* Country comments, ILZSG, Commission of the European Communities, Battery Council International, US Department of Commerce, US Bureau of Mines, Japan Storage Battery Association, Tonatsu Metallurgical Company.

*Source:* Proceedings of the REC '93 International Recycling Congress, "Advances in Recovery and Recycling. Concepts and technology."



**Table 5.8** Summary tables: lead  
total reported consumption by country

	Thousand Metric Tonnes						% change 1992-3
	1988	1989	1990	1991	1992	1993	
<i>Australia</i>	49.3	51.7	46.0	42.6	43.1	51.2	18.8
<i>Austria</i>	61.0	61.0	65.5	66.0	66.0	62.0	-6.1
<i>Belgium</i>	66.1	62.0	67.7	63.5	64.5	66.0	2.3
<i>Brazil</i>	95.5	100.3	75.0	66.0	69.0	74.0	7.2
<i>Canada</i>	88.0	87.7	71.5	79.6	91.7	89.1	-2.8
<i>Finland</i>	12.1	13.2	13.4	12.2	7.0	4.0	-42.9
‡ <i>France</i>	238.2	265.4	263.2	266.3	259.4	240.2	-7.4
‡* <i>Germany</i>	336.9	366.2	375.3	401.0	397.5	362.4	-8.8
** <i>India</i>	51.1	52.9	51.8	53.6	40.2	33.9	-15.7
‡ <i>Italy</i>	252.0	261.0	259.0	259.0	247.0	234.0	-5.3
<i>Japan</i>	406.5	405.7	416.4	422.2	401.3	371.2	-7.5
<i>Korea, Republic of</i>	146.0	155.0	149.0	164.0	164.0	178.0	8.5
<i>Mexico</i>	77.1	85.7	66.8	79.7	92.5	84.0	-9.2
<i>Netherlands</i>	58.4	58.5	62.0	59.0	52.0	48.0	-7.7
<i>New Zealand</i>	7.6	10.0	8.0	5.1	5.1	6.7	31.4
*** <i>Scandinavia</i>	58.4	41.8	36.3	33.0	33.0	41.0	24.2
<i>South Africa</i>	56.1	62.9	65.9	53.9	53.9	52.7	-2.2
**** <i>South East Asia</i>	171.4	172.0	185.0	237.0	237.0	253.0	6.8
<i>Spain</i>	110.9	110.0	126.7	105.0	105.0	104.0	-1.0
<i>Switzerland</i>	10.7	7.9	8.7	7.6	7.6	7.5	-1.3
‡ <i>United Kingdom</i>	339.5	336.4	334.0	302.3	302.3	298.0	-1.2
‡ <i>United States</i>	1245.2	1277.6	1275.2	1240.7	1240.7	1357.1	9.4
<b>Total</b>	<b>3924.8</b>	<b>4044.9</b>	<b>4022.4</b>	<b>4027.7</b>	<b>3979.8</b>	<b>4018.8</b>	<b>1.0</b>

\* Prior to 1991, former Federal Republic only

\*\* Consumption in the Organised Sector

\*\*\* Denmark, Norway and Sweden

\*\*\*\* Taiwan (China), Hong Kong, Philippines, Malaysia, Singapore, Thailand and Indonesia

‡ Data for these countries include total metal consumption in all forms, i.e. refined lead and alloys (lead content), plus remelted lead recovered from secondary materials. Data for other countries include refined lead and alloys only

**Table 5.9** Summary tables: lead  
principal uses

	LEAD CONSUMPTION: THOUSAND METRIC TONNES						% change 1992-93
	1988	1989	1990	1991	1992	1993	
Batteries	2394.3	2492.3	2541.3	2557.8	2565.6	2661.7	3.7
Cable sheathing	183.2	196.0	182.1	169.9	152.5	143.5	-5.9
Rolled and extruded products	312.0	311.8	309.6	284.9	273.2	265.4	-2.9
Shot-ammunition	93.8	98.8	101.3	108.8	113.2	115.4	1.9
Alloys	147.1	141.8	134.4	133.8	139.0	137.8	-0.9
Pigments and other compounds	526.6	557.0	517.0	542.9	530.6	488.9	-7.9
Gasoline additives	103.0	98.2	86.9	74.0	58.1	54.3	-6.5
Miscellaneous	164.8	149.0	149.8	155.6	147.6	151.8	2.8
Total*	3924.8	4044.9	4022.4	4027.7	3979.8	4018.8	1.0

	PERCENTAGES OF TOTAL CONSUMPTION					
	1988	1989	1990	1991	1992	1993
Batteries	61.0	61.6	63.2	64.0	64.5	66.2
Cable sheathing	4.7	4.8	4.5	4.2	3.8	3.6
Rolled and extruded products	7.9	7.7	7.7	7.1	6.9	6.6
Shot-ammunition	2.4	2.5	2.5	2.7	2.8	2.9
Alloys	3.7	3.5	3.3	3.3	3.5	3.4
Pigments and other compounds	13.4	13.8	12.9	13.5	13.3	12.2
Gasoline additives	2.6	2.4	2.2	2.1.8	1.5	1.4
Miscellaneous	4.2	3.7	3.7	3.9	3.7	3.8
Total*	100.0	100.0	100.0	100.5	100.0	100.0

\* Countries included: Australia, Austria, Belgium, Brazil, Canada, Finland, France, Germany, India, Italy, Japan, Republic of Korea, Mexico, Netherlands, New Zealand, Scandinavia, South Africa, South East Asia, Spain, Switzerland, United Kingdom, United States.



### 5.4.5 Comparison of lead-acid battery recycling technologies

**T**his exercise requires a considerable amount of work, and is therefore best done by students with a technical background who have thoroughly studied the background papers. The exercise should be tackled as a project, on which students are allowed to work in small groups over a period of several weeks. It is advisable to organise this project in advance, and maybe get the involvement of some senior students to assist the working groups. The students may need considerable guidance from the trainer as to how detailed the study should be. It requires close involvement of the trainer.

#### NOTE

The result of this exercise should not state a preference for one technology over the other. The comparison of the different technologies should reveal that they can not easily be compared with each other because of factors like accessibility of the market for recycled products, capacity of the technology, local conditions, etc.

However, you can identify the environmental impacts of the different technologies and develop general areas for preferences.

There are various types of lead-acid battery recycling facilities, all using a range of technologies and techniques. As a consequence, the end products and their quality differ depending on the facility where the lead-acid batteries are recycled. End products may vary from scrap and secondary lead, to reusable polypropylene, detergents, refined lead, etc.

The recycling facilities mainly differ from each other in two respects:

#### **1** The wrecking section of the lead-acid battery recycling facility.

The simplest wrecking operations are designed to release only the sulphuric acid. The most advanced wrecking operations separate and recover all the constituents of the battery: acid, PVC, ebonite, polypropylene, lead scrap, and lead paste. In between, there is a range of wrecking operations using different technologies and resulting in different end products (see background papers).

#### **2** The smelting section of the lead-acid battery recycling facility.

The International Lead and Zinc Study Group distinguishes the following smelter types: blast furnace, stationary reverberatory furnace, blast furnace and stationary reverberatory furnace, bergsoe type plant, electric furnace, blast furnace and electric furnace, stationary reverberatory furnace and electric furnace, Kivcet, and Isasmelt process (World Directory, ILZSG, 1994).

This exercise consists of two assignments. The first assignment asks you to make an environmental evaluation of several types of wrecking operations. The second assignment concerns the selection of the most environmentally friendly smelter type. You are asked to choose one of the assignments.



**ASSIGNMENT 1**

**Y**ou are asked to make an evaluation of existing wrecking operations with respect to their general and environmental performance. Find literature in specialized libraries or ask for information about specific wrecking operations at the patent office. Compare two or three wrecking operations, based on a thorough study. At the same time you will have to develop a structured

method of comparing the technologies. Use criteria for capacity, capital investment, energy consumption, emissions, end-products, environmental impacts, occupational health, etc.

Prepare a presentation of the different wrecking operations you studied against the criteria you developed, and give an indication of the environmental impacts of each of the operations.

**ASSIGNMENT 2**

**Y**ou are asked to make an evaluation of existing lead smelting technologies with respect to their general and environmental performance.

Find literature in specialized libraries or ask for information about specific smelting technologies at the patent office. Based on a thorough study, compare two or three smelting technologies, which are also considered by the International Lead and Zinc Study Group. You will have to

develop a structured method of comparing the technologies. Use criteria for capacity, capital investment, energy consumption, emissions, end-products, environmental impacts, occupational health, etc.

Prepare a presentation of the different smelting technologies you studied against the criteria you developed, and give an indication of the environmental impacts of each of the technologies.

## 5.5 Some suggestions for answers

### 5.5.1 Obstacles to a perfect recycling scheme

- Question 1**
- (a) Neglect, lack of awareness of a collection system, the distance to the collector, and the lack of an (economic) incentive may all contribute in preventing consumers from delivering lead-acid batteries to the retailer, collector or drop-off depot.
- (b) Keeping the batteries 'in-house' for a long time may lead to inappropriate disposal of the lead-acid batteries; risks to playing children. Inappropriate storage may lead to accidental breaking of the battery.
- Question 2**
- (a) The constraints include neglect, distance to the battery breaker, and absence of economic incentives (international lead-prices or deposits). These constraints may act in combination with the possible absence of a battery breaker or secondary lead-smelter in the country. In this case, international regulations, geographical distance and cost-benefit of transportation play an important role.
- (b) Leaking of sulphuric acid onto the ground, leading to soil contamination. Exposure of workers to acid and lead when inappropriately stored. Depending on the location of the storage facility, animals and children may come in contact with the batteries, leading to exposure to toxins. With time, there is an increased probability of degradation of the stored batteries because of exposure to the elements, vandalism, and accidents (such as fire). The more batteries that are stored, the more serious the consequences of leaks.
- Question 3**
- (a) Decline in international lead-prices. Distance to secondary lead-smelter in combination with the cost-benefit of transporting a small number of lead-acid batteries (see answer to Question 2a). Note the problem which arises when lead loses its value.
- (b) See answer to Question 2b.

### 5.5.2 Case-study on a lead-acid battery recycling facility

- Question 4**
- (a) When sulphuric acid is allowed to enter the rotary furnace, it causes SO<sub>3</sub> emissions. If the sulphuric acid is removed, less energy is needed to smelt the lead fractions. Sulphuric acid can also be recycled cost effectively.
- (b) The main environmental problem is the formation of acid rain.
- (c)  $\text{PbSO}_4 + \text{Na}_2\text{CO}_3 \rightarrow \text{PbCO}_3 + \text{Na}_2\text{SO}_4$   
See 3.4.4 *Low waste technology for reprocessing battery scrap* in Part 3: *Technical Background Papers* for an explanation of why the lead paste is desulphurized before the smelting process.
- Question 5**
- Weight of used lead-acid battery \* fraction of constituent = kg constituent.
- Question 6**
- See International Chemical Safety Cards, under acute hazards/symptoms, prevention, and effects of long term or repeated exposure.



- Question 7** | Fuel consumption drops from 90kg to 40kg per tonne of scrap. Waste gas drops from 12m<sup>3</sup> to 3.2m<sup>3</sup>/kg fuel. Maximal dust content in cleaned gas is 2.5mg/Nm<sup>3</sup>. Dust content drops from 50% to 35%.  
Reduction of lead in dust per tonne scrap can be calculated as follows:  

$$(1 - (40 \text{ kg} * 3.2\text{m}^3/\text{kg} * 2.5\text{mg}/\text{Nm}^3 * 0.35)) / (90\text{kg} * 12\text{m}^3/\text{kg} * 2.5\text{mg}/\text{Nm}^3 * 0.5) * 100\%$$

$$= 91.7\%$$
- Question 8** | During wrecking operations, 95% of the sulphuric acid is removed, and lime is added to neutralize the residual acid in a ratio of 1.2:1 on a weight basis. Total weight after wrecking section:  
 1 million batteries/year \* 17.2kg/battery ..... 17,200 tonnes of batteries/year  
 Removed sulphuric acid = 0.24 \* 17,200 \* 0.95 ..... 3921.6 tonnes  
 Added lime = 0.05 \* 17 200 \* 1.2 ..... 1032 tonnes  
 Total battery scrap after wrecking operations is:  
 17 200 – 3 921.6 + 1 032 ..... 14 310.4 tonnes  
  
 Input for smelting section consists of 85% from wrecking section, 10% dust and recycling products, and 5% reagents. Total input in rotary furnace is 16 835.8 tonnes. Therefore, the average load of one rotary furnace is:  

$$16\ 835.8 / (5 * 5 * 42 * 2) = 8 \text{ tonnes}$$
- Question 9** | You may want to use the example of the secondary lead smelter given in 3.4.4 *Low waste technology for reprocessing battery scrap* in Part 3: *Technical Background Papers*. One of the exercises in Part 5 focuses on the different wrecking techniques. You may want to do that exercise first.
- Question 10** | (a) The fraction of lead in the rotary furnace will increase. Based on an average capacity of each load of 8 tonnes, the capacity of the plant will increase.  
 (b) The energy consumption may be lower because the plastics are not used as an energy source anymore.
- Question 11** | (a) The risks of transportation (accidents, but also spilling of lead-acid from trucks passing through urban areas). Wastewater containing lead, sulphuric acid and other heavy metals may be discharged into the surface water with inappropriate treatment. Lead emissions during smelting, refining, and ingotting – either through air, water, or crops (see transparency on exposure pathways in Section 3.3). Due to sprinkling of the site to prevent the formation of lead dust, the soil may become contaminated with lead.  
 (b) During malfunction/accidents, the afterburner and emission control equipment may not be able to retain pollutants like sulphuric acid fumes, lead, and SO<sub>3</sub>, and dioxins may be formed due to incomplete burning.  
 Students were asked to investigate the risks associated with each of the constituents of the lead-acid battery as part of Preliminary Exercise 3. The consequences of emissions from secondary lead smelters for human health are also summarized in 3.2.1 *Environmental agency closes down company after finding lead in human blood, cows' meat*; 3.2.2 *Potential environmental and occupational hazard from lead*; and 3.2.3 *Mechanisms for risk reduction of lead in the European Community*, in Part 3: *Technical Background Papers*.



**Question 12** (a) Slags can be used as construction material – for road foundations, etc.  
 (b) The major drawback may be that the heavy metals are not immobilized enough and start leaching, causing soil pollution, or leading to health problems in the buildings where they are used.

**Question 13** There are several possibilities, including using it to preheat the scrap before it enters the smelter; it can also be used to generate energy/electricity, or for heating surrounding buildings.

**Question 14** The concentration in the air should always be below  $0.05 \text{ g/m}^3$ . That means that the ventilation system should be able to remove as much lead dust/time unit as is being generated by the two rotary furnaces. The ventilation system should be able to reach a steady state with a lead concentration in the air of  $0.05 \text{ (g/m}^3\text{)}$ .

- $Q_1$  = flow of dust from smelter ( $\text{m}^3/\text{h}$ ).
- $Q_2$  = flow being ventilated (unknown/h).
- $Q_3$  = flow without lead going into the hall =  $Q_2 - Q_1$ .
- $C_1$  = concentration lead dust in  $Q_1 = 60 \text{ (gram/m}^3\text{)}$ .
- $C_t$  = concentration lead dust in the hall ( $\text{g/m}^3$ ).
- $C_3 = 0 \text{ (g/m}^3\text{)}$ .
- $V$  = volume of the hall =  $3600 \text{ m}^3$ .
- $t$  = time (h).

When time reaches infinity,  $C_t$  should remain  $0.05 \text{ g/m}^3$ .

The concentration at  $t = 0$  is  $0 \text{ (g/m}^3\text{)}$ .

This leads to the following equations:

$$V \frac{dC_t}{dt} = Q_1 C_0 - Q_2 C_t + Q_3 C_3$$

$$\frac{\ln(Q_1 C_1 - Q_2 C_t)}{-Q_2} = \frac{dt}{V}$$

$$C_t = \frac{1}{Q_2} (Q_1 C_1 - \exp\left(\frac{-t Q_2}{V} + \ln(Q_1 C_1)\right))$$

For  $t \rightarrow \infty$ ,  $C_t$  reaches  $0.05 \text{ (g/m}^3\text{)}$ . This leads to the following equation:

$$C_t = \frac{Q_1}{Q_2} C_1$$

From this, it follows that the ventilation capacity  $Q_2 = 1200 \text{ m}^3/\text{h}$ .

- Question 15** | Frequent cleaning of areas contaminated with lead, using methods which do not spread the lead, such as mobile or fixed vacuum cleaning apparatus with high efficiency filters or wet cleaning methods.
- Isolate eating and changing areas from areas of lead work and provide suitable facilities to store food, drink and smoking materials.
  - Do not allow smoking, drinking or eating in work areas.
  - Washing of hands and removal of contaminated clothing before entering eating area.
  - Provide work clothing which can be kept separate from normal clothes.
  - Removal of contaminated clothing and showering prior to leaving the workplace premises.
  - Washing of contaminated clothing at the workplace, so as to minimise the likelihood of spreading the contamination to the home.
  - Make sure that personal protective equipment is properly maintained and stored.
  - Set procedures for regular plant maintenance.
  - Follow operation instructions closely in order to avoid lead dust dispersion during various batch and transfer operations.
- Question 16** | Don't use PVC, because it is not being recycled. Try to use other materials so slags do not contain heavy metals. Design batteries so that they can be repaired rather than recycled.
- The use of PVC separators results in considerable economic and technical problems (difficulties in dust collection, equipment corrosion, necessity of special storages, etc.) during scrap treatment. Replacing these separators with ones which do not contain chlorine cuts the costs for lead production from secondary raw material.
- At the same time, the use of new parts in lead-acid batteries complicates the scrap treatment. For example, the use of copper contact pins instead of lead can make scrap separation difficult, and increases the yield of drosses and matte. The most serious difficulties can be caused by addition to lead alloys of such elements as cadmium, tellurium, or arsenic. These elements and their compounds are more volatile and toxic than lead and its compounds.
- Question 17** | 97.2% of all lead is recycled. Assume that 97.2% of metallic lead and 97.2% of lead from lead paste is being recuperated. Calculate the fraction of lead in lead paste, then calculate the total initial amount of molecular lead. 97.2% of this total can be used for production of new batteries.







# Appendices

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# *Appendix I*

## **Supporting Documents for this Package**

The following documents are available to support further work using this package:

*Promoting Waste Recycling: Part I* [1994]

In *Industry and Environment* Vol. 17, No. 2.

*Promoting Waste Recycling: Part II* [1994]

In *Industry and Environment* Vol. 17, No. 3.

*Gestion de l'environnement dans les usines de recyclage des batteries plomb-acide*

[anticipated publication date 1996] UNEP IE.

*Life Cycle Assessment: what it is and how to do it* [1996] UNEP.





## Appendix II

### List of Training Resource Packages available from UNEP IE

The following training resource packages have been developed by UNEP IE. They all use interactive training methodologies to explain the subject, and are aimed at educators who, although technically skilled, may not have specialized knowledge in this particular area.

The packages are available from UNEP IE.

Some trainers' packages are still under development, and users are encouraged to assist UNEP to bring these to a final stage of publication.

Due to the cost of printing of the packages (between 100 and 400 pages), the completed documents are offered for sale to most users. However, a limited number of draft packages are free of charge to users prepared to contribute to their further development through review, field testing and adding material. Assistance with translation would also be welcome.

*Cleaner Production: a Training Resource Package* [1996] First Edition. Contains background reading, transparencies, bibliography, and work exercises. 110 pages. Price \$120 (English, Spanish). This package can be used with the workbooks below.

*Trainer's Workbook on Cleaner Production in Leather Tanning* [1996] First Edition. Contains background reading, case studies, work exercises and answers. 120 pages. Price \$120.

*Trainer's Workbook on Cleaner Production in the Brewing Industry* [1996] First Edition. Contains background reading, case studies, work exercises and answers. 75 pages. Price \$100.

*Trainer's Workbook on Cleaner Production in Textile Wet Processing* [August 1995] First Edition. Contains background reading, case studies, work exercises, answers, references. 140 pages. Price \$120.

*Management of Industrial Accident Prevention and Preparedness: a Training Resource Package* [1996] First Edition. Contains background reading, case studies and work

exercises. 110 pages. Price \$120. This package also helps to explain the APELL programme.

*Risk Management of Contaminated Industrial Land: a Training Resource Package* [1996] First Edition. Contains background reading, case studies and work exercises. 110 pages. Price \$120. English, Spanish.

*Hazardous Waste, Policies and Strategies: a Training Manual* [December 1991] TR10. Contains background reading, case studies, work exercises, reference tables and bibliography. 250 pages. Price \$120. English, French, Spanish.

*Landfill of Hazardous Industrial Wastes: a Training Resource Package* [March 1994] TR17. Contains background reading, case studies, work exercises, reference tables and bibliography. 315 pages. Price \$120.

*Environmental and Technological Issues related to Lead-Acid Battery Recycling: Trainers Workbook* [1996] First Edition. Contains background reading, transparencies, bibliography and work exercises. 130 pages. Price \$120.

**Environmental Management of Mining Sites: a Training Manual** [1995] UNEP/DDSMS. Contains background reading, transparencies, case studies, work exercises and answers. 200 pages. Price \$160.

**Environmental Management Systems: Training Resource Kit** [1995] UNEP/ICC/FIDIC. Contains background reading, transparencies, case studies, work exercises, bibliography. 492 pages. Price \$190.

**Aerosol Conversion Technology Handbook** [1994] Price FF225/US\$45 for developed countries.

**Training Manual on Chillers and Refrigerant Management** [1994] Price FF425/US\$85 for developed countries.

**Training Manual on Good Practices in Refrigeration** [1994] Price FF400/US\$80 for developed countries.

**Environmental Impact Assessment: a training resource manual** [1996] Preliminary version. Available from UNEP Environment and Economics Department, UNEP, Nairobi.

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# Appendix III

## About UNEP Industry and Environment

**I**ndustry and Environment was established by UNEP in 1975 to bring industry and government together to promote environmentally sound industrial development.

UNEP IE is located in Paris and its goals are to:

- 1 encourage the incorporation of environmental criteria in industrial and development plans;
- 2 facilitate the implementation of procedures and principles for the protection of the environment;
- 3 promote the use of safe and clean technologies;
- 4 stimulate the exchange of information and experience throughout the world.

UNEP IE provides access to practical information and develops co-operative on-site action and information exchange backed by regular follow-up and assessment. To promote

the transfer of information and the sharing of knowledge and experience, UNEP IE has developed three complementary tools:

- technical reviews and guidelines;
- *Industry and Environment*: a quarterly review;
- a technical query-response service.

In keeping with its emphasis on technical cooperation, UNEP IE facilitates technology transfer and the implementation of practices to safeguard the environment through promoting awareness and interaction, training and diagnostic studies.

### Some relevant UNEP IE publications

Refer to Appendix II for trainers' packages. For complete list, refer to publications catalogue.

*Industry and Environment* [quarterly] deals with issues relevant to industrial development, such as auditing, waste management, industry-specific problems, and environmental news.

*Government Strategies and Policies for Cleaner Production* [1994] 32pp.

*Cleaner Production Worldwide* Vol. I and II [1995] 48pp.

*Life Cycle Assessment: what it is and how to do it* [1996] 92pp.

*Audit and Reduction of Industrial Emissions and Wastes: Technical Report No. 7* [1991] UNEP/UNIDO. 127pp.

*Monitoring of Industrial Emissions and Wastes: Technical Report No. 27* [1996] UNEP/UNIDO. 188pp.

*Energy, Efficiency and Climate Change* [1991] UNEP/IPIECA. 95pp.

*Hazard Identification and Evaluation in a Local Community: Technical Report No. 12* [1992] 86pp.

*Health Aspects of Chemical Accidents: guidance on chemical accident awareness, preparedness and response for health professionals and emergency responders* Technical Report No. 19 [1994] A joint IPCS/OECD/UNEP/WHO publication: OECD Environment Monograph No. 81. 47pp.

*Environmental Aspects of Industrial Wood Preservation: a technical guide* Technical Report No. 20 [1994] 105pp.

*The Textile Industry and the Environment* Technical Report No. 16 [1994] 120pp.



*Environmental Management in the Brewing Industry Technical Report No. 33 [1995] 120pps.*  
*Storage of Hazardous Materials Technical Report No. 3 [1990]*  
*Companies Organization and Public Communication on Environmental Issues Technical Report No. 6 [1991] 130pp.*

*Company Environmental Reporting Technical Report No. 24 [1994] 118pp.*  
*From Regulations to Industry Compliance: Building Institutional Capabilities Technical Report No. 11 [1992] 62pp.*

