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Fundamentals of the Recycling of Lead-Acid Batteries

Dr.-Ing. Heino Vest (2002)

Batteries are used whenever electrical energy is needed, but there is neither a direct connection to the public electricity grid nor a generator-based stand-alone supply. Batteries store electrical energy as chemical energy. During discharge, the chemical energy is re-converted into electrical energy. Depending on the

project). If we consider China alone, the most populous country of the world, which currently starts to introduce private car transport, it is obvious that high growth rates in the consumption of starter batteries must be expected in the future, especially in developing countries. Returning used lead batteries to the

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battery system, this improves its lead-acid reversible. There are two types of batteries: 'primary batteries' and 'secondary batteries'.

Lead-acid batteries are called secondary batteries or accumulators since they are rechargeable. They again can be divided into starter and industrial batteries. Starter and industrial batteries are used to provide large quantities of energy (e.g. to start a car, operate electric vehicles, as energy storage medium for solar applications, as short-term emergency power source, etc.). Units generally weigh from a few kilograms to one ton.

In the lead-acid battery sector, starter batteries have by far the largest share. In 1995, approx. 96 million units were produced worldwide (source: Battery Council International). An annual production growth rate of < 2% is expected. Especially in developing countries, where the number of cars is growing over-proportionately, high growth rates in the use of lead-acid batteries are to be expected. Studies carried out in Botswana indicate that the number of batteries used in the automobile sector will grow by 40-50% over the period from 1995 to 2005 (source: GTZ waste management

recycling due to the compactness of a battery, its high lead proportion (>95%) and relatively high metal prices, it has been worth while for consumers to return their own or collected car batteries to the scrap trade or secondary smelters. The return rate of spent batteries was thus already high in times when catchwords such as resource conservation and environmental protection, recycling, closed-loop materials management etc. did not yet play a role. Even today, the success of lead battery recycling in developing countries continues to be determined largely by the potential earnings of scrap collectors and traders. In industrialised countries, statutory requirements to take back spent batteries have compensated for the loss of economic incentives in spent battery return.

In most European countries, battery retailers are under obligation to take back spent batteries. Lead batteries also come from repair workshops, the reprocessing of scrap car bodies and at municipal collection centres. In Germany, for example, this well functioning and effective collection system has led to a return rate of more than 95% for starter batteries and

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almost 100% for industrial batteries. In developing countries, too, return rates of up to 80% can be achieved where buying-up structures for spent batteries are in place. In Zimbabwe (source: Central African Batteries) for example, the entire demand for local battery production is covered by recycling of used batteries.

1. Battery scrap raw material for recycling

The major source of raw material for lead recycling are starter batteries from motor vehicles. Modern car batteries consist of a PP (polypropylen)-casing, plates (grids and paste), connectors/poles and bridges, and PP-separators as insulators between the plates (Fig 1). Paste consists of Pb, PbO₂ and PbSO₄. The electro-chemical reactions which take

Older types of batteries have a hard rubber casing and PVC (polyvinylchloride)-separators instead of casings and separators from PP. In some developing countries (e.g. Zimbabwe) these types of batteries are still produced and in use.

Composition of a 12V-44Ah-210 A-starter battery in a hard rubber casing

lead containing components	58,8%
hard rubber	17,7%
sulphuric acid	26,2%
separators (PVC)	2,3%

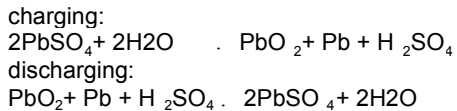
	100,0%

total weight approximately 15 kg

Composition of a modern 12V-44Ah-210 A-starter battery in PP-casing

lead containing components	63,9%
PP-components	5,0%
sulphuric acid	28,6%
separators	

reactions which take place during charging and discharging of lead acid battery are:



(PP,	-----
PVC,	100,0%
total weight	approximately 13-14 kg
2,5%	

Tab. 1: Battery composition

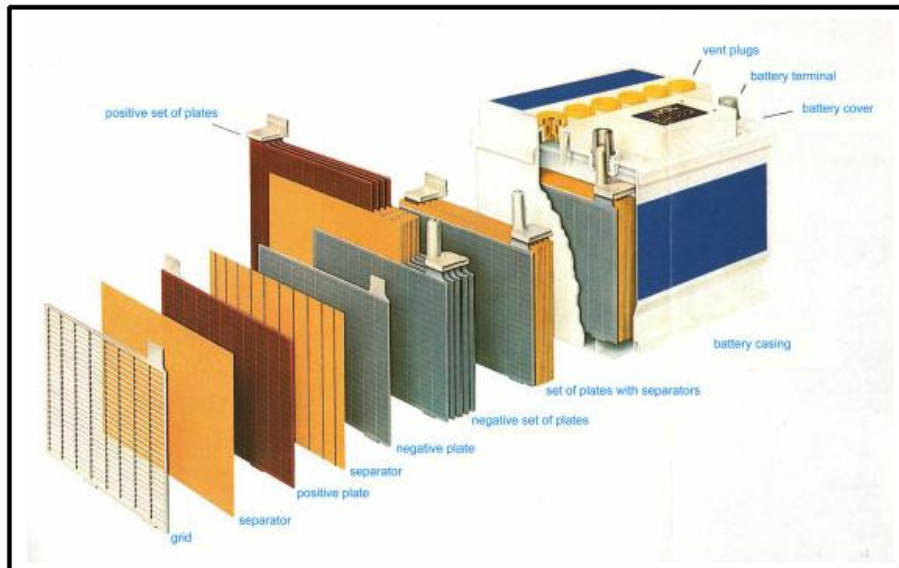


Fig. 1: Design of a starter battery

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Therefore, recyclers have to be aware that batteries in hard rubber casing and PVC-separator will come in with battery scrap.

Depending on the type of battery, its size and design, the material composition of a starter battery varies. Table 1 compares an old type of battery in hard rubber casing with a modern type of battery. The lead-bearing components of a battery are:

Grid metal, poles, bridges	44%
Pb 96-98%	
Sb 2-4%	
(Ca) <0,5%	
Paste	56%
PbSO ₄ 60%	
PbO (PbO ₂) 19%	
PB 21%	
	100%

Tab. 2: Approximate

components of an accumulators like lead, plastics, acids, etc. are at first separated and then processed individually, or the acid is extracted first and the batteries are processed as a whole. In the first case, recycling materials are recovered from all components of a battery. In the second case, only lead is recovered (partially also residual battery acid), whereby organic components are consigned to energy recycling. In view of the high pollution control standards implemented in secondary lead smelters of industrialised countries, modern lead recycling does not pose a significant health hazard to the local population or the environment.

In developing countries spent lead batteries are recycled both in industrial facilities and by informal small enterprises. Industrial recycling smelters use both the grid

Tab. 2. Approximate composition of components of a starter battery

The grids of old types of batteries have a higher Sb (antimony)-content (~4%) than the modern maintenance-free batteries (~2%), which instead add Ca (calcium) <0,5% to their grid alloy.

2. Recycling of lead-acid batteries

2.1 General considerations

As already mentioned, lead-acid battery recycling has a long tradition, especially in industrialised countries. The battery and scrap trade takes back spent batteries free of charge or even pays the metal value. Because the metallic fraction of a battery consists largely of lead, metallurgical reprocessing of battery scrap was never a serious problem. Recently it has been rather the stricter environmental requirements that have caused problems for secondary lead smelters and made lead recycling less economically viable.

Lead recovery from spent accumulators can take two basic routes. Either the

grid produce secondary lead. The informal sector, in contrast, often only uses the metallic parts of old batteries (grids, lead terminals, bridges) to produce articles such as solders or weights for fishing nets. The other parts of the battery are simply dumped in the environment.

Even industrial recycling facilities in developing countries employ many manual techniques due to cheap labour. Batteries are often broken up, emptied, separated and charged to the furnaces by hand. The lead extracted is refined and cast into ingots manually. This creates a potential hazard for the workers, the surrounding population and the environment (soil, ground, water resources, etc.) in general.

Some secondary smelters also buy up pre-sorted battery fractions, e.g. grids and lead paste without casings and separators, in addition to complete batteries. The lead smelters thus save several processing stages and do not have to deal with casing and separator wastes. They are therefore willing to pay a higher price for the material supplied. This practice is very harmful in environmental terms. Through the

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containing residues and wastes arise in many places and it becomes impossible to control their proper disposal.

2.1 Metallurgical aspects of lead recycling from battery scrap

As described before, the lead bearing raw materials extracted from lead-acid battery scrap are:

Pb(Sb) metal from grids, terminals and bridges

PbO (PbO₂) lead oxides, part of the paste

PbSO₄ lead sulphate, part of the paste

While the first component needs only melting, the two other components have to be converted by

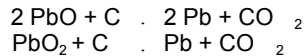
form of coal) and iron (in the form of iron swarf). Impurities are collected in the slag which requires for example soda ash as liquidifying and slag forming constituent. The product of the smelting operation is crude lead, which needs subsequent refining, and soda slag as residue. Since soda slag is water soluble and therefore hazardous when brought to landfills, modern lead recycling plants use silica slag (fayalite slag), which is water insoluble. It requires, however, a much higher furnace operation temperature of approximately 1400C.

The refining of crude lead takes place in a refining kettle at temperatures between 400 and 550C. If only battery scrap is used for lead production, two subsequent refining steps are required:

1

be converted by
 processes to obtain lead metal, which
 takes place in the furnace.

The first type of chemical reaction
 converts PbO (PbO₂) into Pb through a
 reduction process:



The second type converts PbSO₄ into
 PbS, again through a reduction process:



Finally PbS is converted into Pb through
 the following reactions:



or



The above mentioned chemical reaction
 are sum reaction. That means that there
 are intermediate steps in between. The
 reactions take place in the melting furnace
 at high temperature (900-1200 C) and
 need additives, which

1.

Removed the melts through copper
 of wires.

2. Removal of antimony originated from
 which the former grid metal to produce pure
 might lead
 have

While the removal of Cu is done in adding
 elementary sulphur, Sb can be removed
 by selective oxidation or by adding sodium
 nitrate (NaNO₃). The lead in the kettle is
 stirred and a dross formed. The impurities
 are now removed from the melt by
 skimming of the dross formed. It is obvious
 that the success of the refining has to be
 controlled by chemical analysis. The
 refined metal is cast into ingots for
 shipment, sale or further manufacturing.

2.3 Technical steps in battery recycling

In developing countries lead-acid battery
 scrap is normally processed in rotary drum
 furnaces using liquid fuel as energy
 source. Lead bearing feed materials are
 either whole battery packs (grids and
 paste) where the separators have been
 removed or two separate fractions

are carbon (in the

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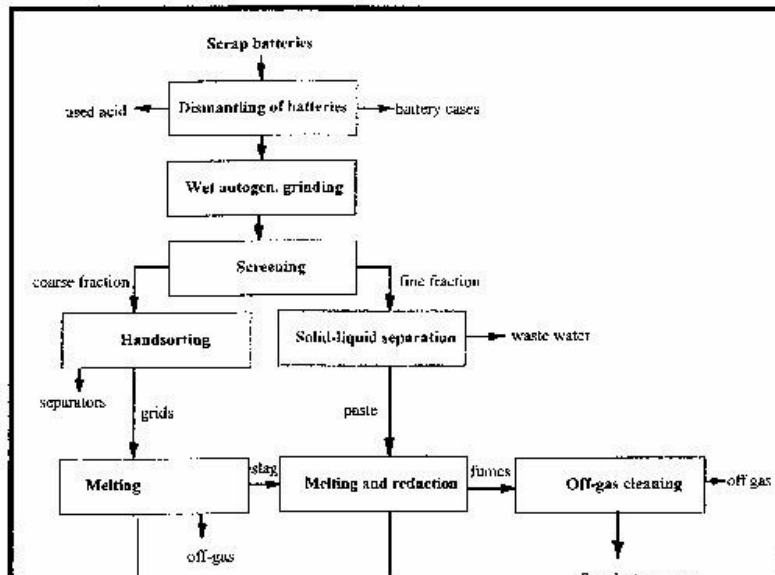
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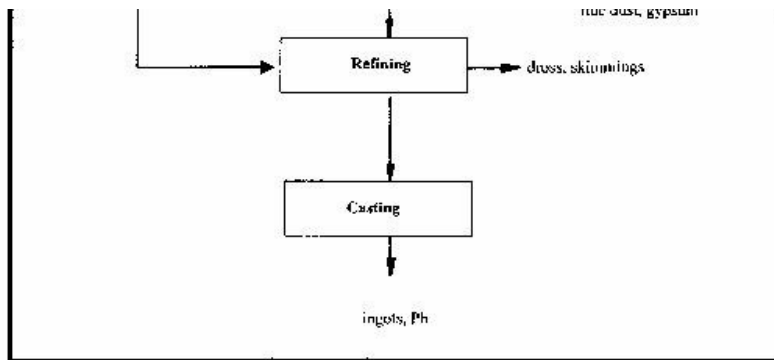


Fig. 2: General flow sheet of a semi-mechanised battery scrap recycling

a) grid metal only and b) paste and other fines

The flow sheet in Fig. 2 shows a semi-mechanised process option for small to medium scale battery recycling in developing countries. In this option grids and paste are separated and individually processed. Since the grids (2/5 of the total material) are already in the metal stage, metallurgical process of converting

they do not need to go through the whole PbO/PbSO₄ into lead metal. They only need to be molten at some 500C (low temperature melt), refined and cast into ingots. Thus, energy and time are saved.

2.3.1 Dismantling of battery cases and feed preparation

Used batteries are emptied by hand and the acid is collected in plastic barrels. If the full barrels are kept motionless for some time, solid impurities will settle at the bottom of the barrels. This process of sedimentation may be assisted by adding some

5 flocculent.

The
purified
acid
is
then

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decanted and packed for sale. Possible customers for the recycled acid is the mining and metallurgical industry which uses acid in various leaching operations. The remaining battery sludge is neutralised with lime. After passing through a filter press the filter cake may be charged together with the fine fraction into the melting and reduction furnace.

In a next step the tops of the acid-free batteries are cut off by a guillotine shear and the grid packs are removed from the battery case. They are fed to a perforated grinding drum, which rotates in a water basin. By moving the feed in the drum an autogenous grinding process starts which separates the grids from the separators and, more important, the paste from the grids. At the same time the perforation of the drum acts as a sieve. The fines are separated and carried

hammer mill (Fig. 3) and fed to a grinding/washing drum for separation.

In both cases, the slurry is pumped continuously or batchwise to sedimentation tanks, where the solids settle at the bottom. The clarified liquid is returned back to the grinding operation, while the sludge at the bottom of the tanks passes a filter press or is left to sun-dry. The filter or sun dried cake is the main feed for the melting and reduction operation which will produce almost pure lead.

The second fraction the coarse material (basically grids and separators) leaves the grinding drum at its lower end. Separators and grids are separated from each other by hand sorting using a slow moving transmission belt (Fig. 4). The metal

separated and carried
 away by the water. The water neutralises
 the acidic solutions and prevents the drum
 from massive corrosion.

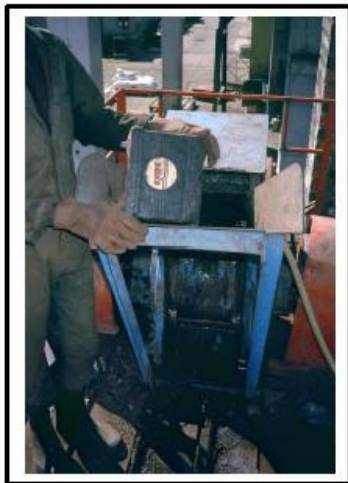


Fig. 3: Hammer mill crushing whole Batteries

Instead of this labour intensive method whole batteries may be crushed in a

metal
 fraction
 temperature melt producing a PbSb-alloy.
 is
 the
 main
 feed
 for
 the
 low

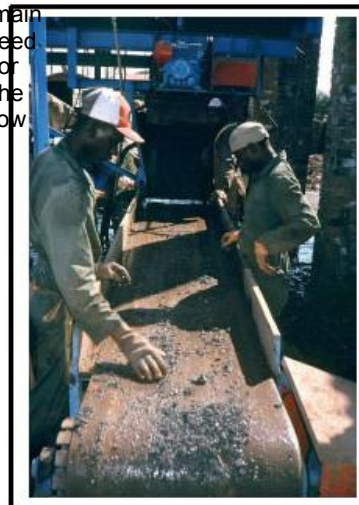


Fig. 4: Hand sorting of coarse feed fraction

Empty battery cases and covers with the attached poles, bridges and remaining grid parts are charged to a wet hammer mill, where metal parts and remaining paste are separated from the plastic. The output

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of the mill passes a perforated drum, where solids and slurry are separated. While the solids (metal and plastic parts) are hand sorted, the slurry with the fines is added to the slurry obtained from the grinding drum. The solid metal parts supplement the feed of the low temperature melt.

The plastic residues of the dismantling operation either have to be dumped (in the case of PVC-separators) or can be used as fuel (PP, cellulose, hard rubber) in cement factories. In this case it is important that no lead remains in the plastic product.

2.3.2 Melting and reduction operation of paste and battery fines

The filter or sun baked

temperature the combustion air should be preheated.

Depending on the temperature and the amount of feed material in the furnace, the reaction time will be 2-3 h. Due to the difference in specific weight the molten lead produced settles at the bottom part of the furnace. When enough lead has accumulated, it is tapped into a mobile ladle and transported in liquid stage to the refining kettle.

With less PbO/PbS in the slag and more Pb-metal produced the viscosity of the slag increases. This hampers the separation of the small Pb-droplet from the slag. To overcome this problem either more soda ash has to be added or the temperature in the furnace must be increased. Both solutions have negative effects.

The filter of sun baked charge of pastes is charged into a short rotary drum furnace (Fig. 5) where the charge is melted together with slag forming constituents (soda ash = Na_2CO_3) and reaction additives (Fe-swarf, coal). The ratio of the feed materials Pb-fines : Fe-swarf : Soda ash : coal is approximately 10:2:1:0,5. The energy needed for the process is obtained from the burning of the coal within the furnace and by an additional burner running on heavy fuel oil, paraffin,

effects. While the amount of slag which finally needs to be discarded, the second measure leads to a first higher energy consumption and even a first evaporation of lead into the off-gas increases

It is more advisable to tap the lead before the optimum of recovery is achieved and to leave the remaining lead-rich slag in the furnace for a second or third cycle with new feed material.



Fig. 5: Rotary drum furnace for battery scrap recycling

diesel, waste engine oil, etc. To save energy and to achieve a higher furnace

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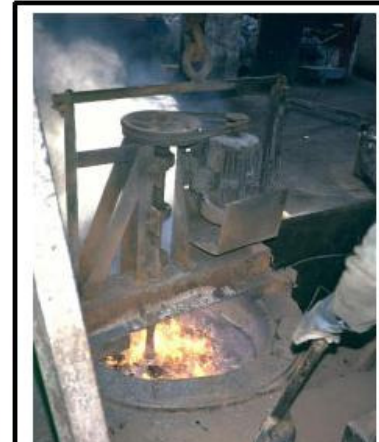
After a number of production cycles the amount of slag in the furnace will be too large to continue the operation. By adding a bit more coal and fresh soda ash a slag with a low Pb content (<9% Pb) can be achieved which is then tapped from the furnace together with the finally produced lead. While the lead metal is forwarded for refining the slag has to be dumped.

Off-gas and flue dust from the operation is sucked of and treated in the off-gas cleaning system.

2.3.3 Melting of grids, terminals and bridges

The coarse fraction of the crushed battery scrap is fed to a crucible furnace, melting kettle or rotary drum furnace. By adding a bit of soda ash the

Zn, Sb, As) is formed and skimmed off. This de-copperisation step should be carried out at least two times to secure the refining result.



bit of soda ash the charge is melted while. During this operation insoluble impurities will settle on top of the melt and join the soda ash slag, which is skimmed off at the end of the melting operation. Gases and flue dust from the process are soaked away and passed over to the gas cleaning system.

The melt is cast into ingots or transferred in liquid stage to the refining kettle.

2.3.4 Refining of crude lead

First, the lead tapped from the furnace has to be cleaned from residual oxides and slag. For that purpose a bit of pitch and saw dust is added. After stirring for a while the impurities settle at the surface and are skimmed off (Fig. 6).

Crude lead originating from battery scrap is normally alloyed with copper and antimony (with traces of Ca, Sn, As, Zn). In order to remove the unwanted elements two further refining operations have to be carried out. By adding sulphur to the lead melt and after stirring for some time, a Pb/Cu₂S-dross (and if present



Fig. 6: Refining of crude lead in a kettle

The de-copperised lead still contains a large amount of antimony (and maybe some Sn, As). All of these elements can be removed by oxidation. For that purpose air or oxygen-enriched air is blown into the melt and stirred. The different oxides formed settle at the surface and can be skimmed off. The oxidising process is completed when mainly lead oxide is formed.

Instead of oxidising the impurities by injecting air, sodium nitrate (NaNO₃) can be added. Here again a dross containing the impurities (and lead) is formed, which is skimmed off afterwards. All refining by-products or residues should be processed to recover lead and other valuable components.

The refining processes and the purity of the refined lead are monitored by chemical analysis.

with minor parts of

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The off-gases of each of the processes are collected and fed into the central gas cleaning system of the plant.

2.3.5 Gas cleaning system

Due to the lack of environmental legislation and monitoring, and due to lack of funds industrial operations in developing countries often have very poor emission control and off-gas cleaning systems. Because of the hazardous potential of the majority of the elements and compounds which are involved in lead smelting and refining (Pb, Sb, As, SO₂, etc.), a certain gas cleaning standard must be achieved and should be compulsory.

Therefore, all fumes, gases and dusts which are generated during the different production steps should

wet gas cleaning system which consists of a venturi washer and a wet scrubber.

The task of the venturi washer is the collection of the fine dust particles. Water and off-gas is mixed under high turbulence and gas/water spray velocity, forming a fine slurry, which is pumped to a sedimentation tank.

The more or less dust free off-gas afterwards enters a wet scrubber. Here, the main task is the removal of the SO₂-gas of the off-gas. By adding lime to the scrubber liquid, the SO₂ in the off-gas will react with the lime water forming gypsum. The gypsum is insoluble in water and precipitates. Again, the fine slurry of the second scrubber is pumped into a sedimentation tank. The clean gas leaves the whole process via the main chimney.

production steps should be treated in a central gas cleaning system. A standard off-gas treatment system normally consists at least of a hot dust chamber and/or hot cyclone, a venturi washer and a wet scrubber (Fig. 7).

iii
lime and flocculent neutralise the slurry and assist the sedimentation of the fines. tank small amounts



Fig. 7: Off-gas cleaning system of a lead recycling furnace in Zimbabwe

From the furnace the hot gases pass through a hot dust chamber and/or a hot cyclone where most of the coarse dust particles are separated from the gas stream. From there the off-gas feed into a

The sludge passes a filter press producing a filter cake. The extracted water is re-circulated to the scrubbers while the filter cake is fed back into the melting and reduction furnace.

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3. Environmental considerations

As already mentioned, the potential health and environmental risk involved when processing battery scrap is very high. Depending on the level of mechanisation and environmental standards, the following environmental hazards can arise:

soil and groundwater contamination by acid spilled when batteries are emptied
 wind dispersal of lead dust if crushed battery scrap is stored without protection
 substantial atmospheric emissions (e.g. lead-containing dust, soot, SO₂, chlorides, dioxins, etc.) when battery scrap is smelted due to:

- processing the entire battery including its organic parts (casing, PVC separators in older battery

- inadequate removal of gases and vapours during the smelting and refining process
- absent or inadequate flue gas treatment

use of water-soluble soda slag without the corresponding landfill design that would prevent leaching and dust formation

open storage of slag and ashes of the refining process

open tipping of residues and wastes such as battery casings and PVC separators.

Workers, too, are exposed to raised levels of harmful substances in such facilities. This generates considerable health risks if appropriate precautionary measures are not taken (respiratory equipment, washing facilities, separate eating and resting

types)

rooms,
regular
examinations,
etc.).

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www.eea.dk European Environmental
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