WASTE OF OLD BATTERIES AND ACCUMULATORS

RELEVANCE OF WASTE STREAM

- Waste products that cause severe environmental damages to soil and water when improperly disposed, separate collection and material recovery shall be applied to avoid that
- EU directive 2006/66/EG about batteries and accumulators stipulates legally binding requirements on collection and treatment and obliges producers to carry out their producer's responsibility

COMPOSITION/MAIN MATERIAL COMPONENTS

Batteries are divided into primary batteries (one-time use) and secondary batteries (repeated use through charge). Various electrochemical functionalities are available at the market. Table 1 presents currently usual types of batteries, their composition and characteristics:

Table 1: Approximate composition of waste oil

<table>
<thead>
<tr>
<th>Type of battery</th>
<th>Applied chemical system</th>
<th>Main components</th>
<th>Capacity (mAh)</th>
<th>Nominal voltage</th>
<th>Durability</th>
</tr>
</thead>
<tbody>
<tr>
<td>Batteries (Primary batteries)</td>
<td>Alkaline-Manganese (AlMn)</td>
<td>Manganese dioxide, Iron, Zinc</td>
<td>~ 2.800</td>
<td>1.5 V</td>
<td>1 cycle</td>
</tr>
<tr>
<td>Zinc-carbon (ZnC)</td>
<td></td>
<td>Manganese dioxide, Iron, Zinc</td>
<td>~ 1.200</td>
<td>1.5 V</td>
<td>1 cycle</td>
</tr>
<tr>
<td>Lithium (Li)</td>
<td></td>
<td>Iron, Manganese dioxide, Lithium</td>
<td>~ 3.000</td>
<td>1.5 V</td>
<td>1 cycle</td>
</tr>
<tr>
<td>Accumulators (Secondary batteries)</td>
<td>Lithium-ion (e.g. with Li-NMC, Li-NCA, Li-LFP as cathode material)</td>
<td>Graphite, Cobalt, Nickel, Manganese</td>
<td>~ 2.400</td>
<td>3.6 V</td>
<td>Up to 1,000 cycles</td>
</tr>
<tr>
<td>Nickel-metal hydride battery (NiMH)</td>
<td></td>
<td>Nickel, Iron, Rare earth</td>
<td>~ 2.200</td>
<td>1.2 V</td>
<td>Up to 1,000 cycles</td>
</tr>
<tr>
<td>LSD-nickel-metal hydride battery (LSD-NiMH)</td>
<td></td>
<td>Nickel, Iron, Rare earth</td>
<td>~ 2.000</td>
<td>1.2 V</td>
<td>Up to 1,000 cycles</td>
</tr>
<tr>
<td>Nickel-cadmium-battery (NiCd)</td>
<td></td>
<td>Iron, Cadmium, Nickel</td>
<td>~ 600</td>
<td>1.2 V</td>
<td>Up to 1,500 cycles</td>
</tr>
<tr>
<td>Rechargeable alkaline-manganese battery (RAM)</td>
<td></td>
<td>Zinc, Manganese</td>
<td>~ 1.800</td>
<td>1.5 V</td>
<td>Minimum 25 cycles</td>
</tr>
</tbody>
</table>

Batteries that contain mercury have a decreasing share on the sales market, because in 2015 a placing on the market of these batteries with more than 0.0005 per cent per weight of mercury has been prohibited. Nevertheless, batteries containing mercury are still in circulation and will be part of the waste management in the future. In Germany, about 1.5 tons per year of mercury were recovered from batteries and button cells.

Recommendations support the application of lithium-ion batteries as efficient option in the area of energy supply of batteries and accumulators.

EUROPEAN LEGISLATION AND REFERENCE DOCUMENTS

The legal framework for the safe handling and disposal of used batteries and accumulators in the countries of the EU is provided through Directive 2006/66/EG of September 6, 2006. This directive replaces a number of former directives issued on the same subject.

Being considered potentially hazardous due to heavy metal concentrations and other hazardous components they contain, old batteries and accumulators are also given special attention in the national regulations of many countries outside the EU.
### Needs and Principal Requirements for Handling the Waste Stream

Best Practice in managing this kind of waste as being determined also by the above directive means to adhere to certain standards concerning hazardous content when introducing battery products on the market and in handling them once becoming a waste.

**Production and marketing:**
A ban on the marketing of batteries and accumulators containing more than 0.0005 mass-% of mercury or 0.002 mass-% of Cadmium provides the basis for the further penetration of these substances into the market and for a stepwise reduction of heavy metal concentrations in the municipal solid waste in Europe (Accumulators used for special systems/items such as alarm systems or emergency lighting are excluded from the cadmium restriction).

**Handling of old batteries and accumulators:**
Batteries and accumulators shall be collected separately from household waste and other waste streams to achieve a high recycling quota. The installation of separate take-back systems for old batteries and accumulators has proven to be a very effective collection system.

In Germany, producers of batteries and accumulators are legally obliged to transfer their producer responsibility to a take-back system: This is possible through the participation in a common, non-profit and comprehensive take-back system or through the installation of an own, producer-specific take back system of one or more producers. Additionally, producers of vehicle batteries and industry batteries shall offer an acceptable take-back option to their distributors free of charge. The transfer of these duties to existing take-back systems as well as the establishment of producer specific take-back systems is possible, too.

It is recommended to establish a central register that monitors, controls and publishes producers that are active at the market to create transparency for all participants. Producers shall transfer information about their brand, the amounts put on the market as well as information about their realisation of their take-back obligations to the register. Additionally, producers should ensure that the transport (partially hazardous materials), the sorting of battery mixtures, the treatment and the recycling is conducted according to state of the art technologies.

No costs should incur for private end users to achieve a high as possible participation quota. It also should guaranteed that private end user are sufficiently informed by producers about

- the meaning of labels/symbols printed on the batteries, e.g. the meaning of toxic substances subject to labelling, which are contained in the producer's batteries
- the legal obligation of end users to deliver old batteries and accumulators at official collection points to make them available to an adequate recycling
- the possibility of a take-back free of charge at sale points of the producers

The labelling of each battery and accumulator with the following symbol sensitize end user about the necessity of a separate collection and the importance to make old batteries and accumulators available to a secure disposal system.

#### Appropriate Collection Strategies and Schemes

Take-back and special collection schemes are the most common ways for the collection and recovery of used batteries and accumulators. Take back can be most efficiently realised via the stores and vendors who are selling batteries, thru public amenity sites and recycling stations of the municipalities or by pick-up arrangements between recycling companies and the (commercial) users, or thru dedicated collection campaigns (in the municipalities).

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**Figure 1:** Label for separate collection of old batteries and accumulators

- [Image of battery label]

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It is recommended that take-back partners make use of special containers to draw attention on and facilitate the separate collection and safe storage of the used batteries/accumulators in their premises. Moreover, the damage of batteries can be prevented at an early stage because collection containers can be exchanged and don't have to be transfilled. Damaged batteries can cause short circuits, which may lead to fires during transportation.

Figure 2: Collection container for used lithium batteries (picture source: INTECUS GmbH)

It is conceivable that public waste management systems voluntarily take part in the take-back system or even being committed to take part in the take-back system by law.

**APPROPRIATE TREATMENT AND RECOVERY SCHEMES**

Due to the fact that the batteries are rarely collected according to their composition, a sorting is necessary before their recycling. Before any sorting the batteries are automatically classified by size, in this way round cells are being excluded from the processing. For the further sorting the following procedures are known:

- **Electromagnetic process**
  First batteries are separated into magnetic (about 85%) and non-magnetic ones. The magnetic batteries are then passing a magnetic field which changes in dependence from the electro-chemical system contained in the battery. Up to six batteries can be identified and sorted per second in such processes. The achieved purity of the sorted fractions reaches 98%.

- **Radiographic process**
  The batteries pass a radiographic (X-ray) sensor. On the basis of the different grey shading produced on the image the electro-chemical system contained in the battery can be identified. Up to twenty batteries can be identified and sorted per second in such processes. The achieved purity of the sorted fractions goes beyond 98%.

The producers of alkaline-manganese batteries and zinc-coal batteries mark their products with a special UV-code in order to achieve a separation of batteries containing mercury and such without this element. This code can be automatically read by an UV sensor.

As an alternative for the above automated sorting processes also a manual sorting can be applied on lower quantities of spent battery products. Provided that adequate safety measures are fulfilled, this is a sufficiently reliable separation method for different types of used batteries, too. The obligatory imprints on battery content do facilitate that kind of sorting process.

Sorting and recycling operations are normally performed separately to allow for the recycling of batteries, whereby the recycling process should be subject to minimum requirements regarding efficiency and process application. In Germany an information/documentation duty of operators of recycling facilities was introduced to a central register, to control and to develop recycling procedures.
Different metallurgic processes can be used for the various electro-chemical systems of batteries. They can be roughly distinguished into pyro- and hydro-metallurgic processes of which relevant examples shall be briefly described hereafter. The main process differences can be characterised as follows:

<table>
<thead>
<tr>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Pyro metallurgic process</strong></td>
<td><strong>Hydro metallurgic process</strong></td>
</tr>
<tr>
<td>- High speed of reaction</td>
<td>- Very selective reactions (high purity of output)</td>
</tr>
<tr>
<td>- High efficiency</td>
<td>- Well controllable for input of stable composition</td>
</tr>
<tr>
<td>- High throughput rates</td>
<td>- Little problems with emissions</td>
</tr>
<tr>
<td>- Suitable for complex compounds</td>
<td></td>
</tr>
<tr>
<td>- Less sensitive to changing input</td>
<td></td>
</tr>
<tr>
<td>- Less selective reaction (lower purity of output)</td>
<td>- Slower speed of reactions</td>
</tr>
<tr>
<td>- Process steps may have to be reiterated several times</td>
<td>- Lower efficiency and throughput</td>
</tr>
<tr>
<td>- High noise and emission potential</td>
<td>- Sensitive against changing input</td>
</tr>
<tr>
<td>- Process residues may cause problems during disposal</td>
<td></td>
</tr>
</tbody>
</table>

**Alkaline-Manganese and zinc-coal batteries**

a) *Roll Furnace* – the roll furnace process is a melting technology where zinc-containing batteries are fed (together with sand and coke) into a rotary kiln. The zinc oxidises and evaporates at a temperature of 1300°C. After cooling down, the oxides are being collected and given away to a primary zinc smelting plant to produce virgin zinc from it. The produced slag can be used in road construction. The general process scheme for the utilisation of used batteries in a roll furnace is shown hereunder.

Figure 3: Process scheme of a roll furnace procedure

b) *Imperial-Smelting-process* – this process generates zinc in metallic form. Also here the zinc gets evaporated and forwarded to a condenser where it is cooled down in mists from lead. The zinc sticks to the lead. Both metals get cooled and separated again. The lead is returned to the condenser while the pure zinc is being gathered and given to refining and new production.
c) Further processes – Further processes for the material recycling of alkali-manganese and zinc-coal batteries are available for

- Electrolytic steel furnace producing steel
- Electrolytic steel furnace producing ferromanganese
- Converter steel furnace producing ferromanganese
- Revolving hearth furnace

Like in the aforementioned processes the zinc is evaporated and recovered from the material mix. The processes are less common, however.

- Dismantling process: Alkaline-manganese batteries of type C and D are mechanically opened and afterwards dismantled. The products of the dismantling process are zinc oxide, iron and manganese oxide.

**Nickel-Cadmium (NiCd) batteries**

Used nickel-cadmium accumulators can also be thermally recycled. Here the cadmium is being extracted (distilled) under a vacuum or inert atmosphere. The remaining steel-nickel mix is given to steel production. Due to the small remaining quantity of such batteries, the already existing capacities in Europe are considered sufficient for the entire continent. One application, the Accurec process, is shown in the scheme hereafter.
Lead accumulators

There are basically two ways of recovering lead from used accumulators. Either the batteries are treated prior to a smelting process and separated by material category (lead, plastic, acid etc.) or they are processed directly as such, after the acid has been removed from the accumulator body. After the liquid acid is drained off, the complete batteries are fed into a blast furnace without further treatment. In the furnace they are smelted in a mixture containing coke, limestone and iron. These additives promote the smelting and transformation processes in the furnace and help to recover the lead step-by-step, and to cleanse it of impurities. The result is crude or raw lead. The process is a.o. employed by the battery producer VARTA under the name (VARTA) Schachtofen-Verfahren [shaft furnace process]. Also a product of the shaft furnace process is the off-gas. It contains the gaseous components of the smelting process: in addition to carbon dioxide and carbon monoxide, dust particles with high lead content and residues from pyrolysis of the plastics. In order to clean the off-gas effectively, its organic content is first burnt off completely. Gas burners heat the off-gas from an initial 200° C to temperatures of up to 1100° C to remove even the last remnants of organic components. After cooling, the gas passes through a filter system which collects almost 100 per cent of the dust content. The collected dust contains about 65 per cent of lead, which makes it a valuable raw material. After a pre-treatment it is returned to the smelting process.

The company BSB Recycling uses the Engitec-technology to recycle lead accumulators from the automotive and industry sector. As a product of the process plastic flakes, soft lead, PbCa-alloys, antimonial lead, special alloys and tin-lead alloys are recovered (Figure 6).

Figure 6: Process scheme of lead accumulators (modified according to BSB Recycling GmbH)

Nickel-metal hydride (NiMH) batteries

The utmost attention in the recycling of this battery type is given onto the recovery of the element nickel. One of the processes currently in use is based on a comminution under vacuum from which a premature nickel substance is obtained for further processing. Due to the possible release of hydrogen during this treatment, a protected atmosphere (vacuum) need to be created. The principle can be seen in the following scheme for the NIREC process. The obtained nickel product is highly sought from steel production for the creation of special alloys.
Lithium batteries
The focal attention in the recycling of lithium batteries is on the recovery of nickel, iron and manganese. The corresponding processes are yet under development. The general principle is shown in the following figure.

Batteries containing mercury (round cells)
The mercury is recovered with the help of the ALD process which is based on a vacuum-thermal treatment. In special, airtight encapsulated installations the mercury will be evaporated at 350°C and 650°C and later on it condenses at lower temperatures. The pure mercury and the mercury free steel obtained in the process can be further utilised in production. The process can be characterised by the following scheme.
In Germany the collection of old batteries and accumulators takes place in the frame of the producer's responsibility. In 2014, more than 170,000 collection points were installed and emptied by following 4 take-back systems:

- GRS Foundation (GRS Batterien - Stiftung Gemeinsames Rücknahmesystem Batterien) [www.grs-batterien.de](http://www.grs-batterien.de)
- producer specific take-back system REBAT, [www.rebat.de](http://www.rebat.de)
- producer specific take-back system ERP Deutschland [www.erp-recycling.de](http://www.erp-recycling.de)
- producer specific take-back system Öcorecell [www.ifa-gmbh.com](http://www.ifa-gmbh.com)

The take-back systems have to ensure a minimum collection quota of 40% per year, which will increase to 45% in 2016. In 2014 about 19,142 tons of batteries and accumulators were collected in total.

Facilities doing the recycling and utilisation of used batteries and accumulators operate in Germany in larger number. Reference plants for some of the processes described above are for example:

### Table 3: Reference facilities

<table>
<thead>
<tr>
<th>Application</th>
<th>Revolving furnace</th>
<th>Imperial-smelting-process</th>
<th>Converter furnace</th>
</tr>
</thead>
<tbody>
<tr>
<td>Location</td>
<td>Goslar</td>
<td>Duisburg</td>
<td>Duisburg</td>
</tr>
<tr>
<td>Input of batteries</td>
<td>5%</td>
<td>2–3 %</td>
<td>2–3 %</td>
</tr>
<tr>
<td>Products</td>
<td>zinc oxide, slag</td>
<td>zinc, slag</td>
<td>zinc dust, lead, slag, iron</td>
</tr>
</tbody>
</table>

Other provider firms for service concerning battery recycling or utilisation are for example:

- Recycling of AlMn and ZnC batteries as well as NiMH batteries: Redux GmbH, Dietzenbach [www-redux-gmbh.de](http://www-redux-gmbh.de)
- Recycling of button cells containing mercury: REMONDIS QR GmbH, Dorsten [www.remondis-qr.de](http://www.remondis-qr.de)
- Recycling of NiCd batteries and batteries containing lithium: Accurec GmbH, Mülheim/Ruhr [www.accurec.de](http://www.accurec.de)
- Recycling of lead accumulators: BSB Braubach der Berzelius Metall GmbH, Braubach [www.berzelius.de](http://www.berzelius.de)
  HOPPECKE Metallhütte GmbH & Co. KG, Brilon [www.hoppecke.de](http://www.hoppecke.de)