Recycling of spent batteries
Christian Ekberg and Martina Petranikova

Waste is what is left when imagination fails
Commercial
One of the challenges of battery recycling is that batteries are both so similar and so different to humans.

As humans, batteries exist in all shapes, colours and sizes.

However, as opposed to humans, they often look very different within
Why recycle batteries at all?

They contain significant amounts of non-renewable resources in the form of chemical elements.

There are laws making it mandatory.
## Battery waste versus virgin ore

<table>
<thead>
<tr>
<th>Battery type (portable ones)</th>
<th>Metal</th>
<th>Metal content in the battery [kg/t of waste]</th>
<th>Metal content in the ore [kg/ ton of the ore]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkaline batteries</td>
<td>Zn</td>
<td>160-200</td>
<td>30-100</td>
</tr>
<tr>
<td></td>
<td>Mn</td>
<td>370-400</td>
<td>300-500</td>
</tr>
<tr>
<td>Zn-C batteries</td>
<td>Zn</td>
<td>270-300</td>
<td>30-100</td>
</tr>
<tr>
<td></td>
<td>Mn</td>
<td>230-250</td>
<td>300-500</td>
</tr>
<tr>
<td>Ni-Cd batteries</td>
<td>Fe</td>
<td>400-450</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ni</td>
<td>220-250</td>
<td>&gt; 10</td>
</tr>
<tr>
<td></td>
<td>Cd</td>
<td>150-170</td>
<td></td>
</tr>
<tr>
<td>Li-ion batteries</td>
<td>Co</td>
<td>250-300</td>
<td>&gt; 10</td>
</tr>
<tr>
<td></td>
<td>Ni</td>
<td>110-120</td>
<td>&gt; 10</td>
</tr>
<tr>
<td></td>
<td>Cu</td>
<td>120-130</td>
<td>&gt; 10</td>
</tr>
<tr>
<td>Lead batteries</td>
<td>Pb</td>
<td>720-730</td>
<td>100-200</td>
</tr>
<tr>
<td>Ni-MH</td>
<td>Ni</td>
<td>600</td>
<td>&gt; 10</td>
</tr>
<tr>
<td></td>
<td>Co</td>
<td>80</td>
<td>&gt; 10</td>
</tr>
<tr>
<td>Rare earth elements</td>
<td></td>
<td><strong>75!</strong></td>
<td>~10g!</td>
</tr>
</tbody>
</table>
How much do the batteries take of production today

<table>
<thead>
<tr>
<th>Metal</th>
<th>% of metal market consumption</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cobalt</td>
<td>50% (predicted to be 60%)</td>
</tr>
<tr>
<td>Zinc</td>
<td>10%</td>
</tr>
<tr>
<td>Nickel</td>
<td>4%</td>
</tr>
<tr>
<td>Lithium</td>
<td>40% (predicted to increase)</td>
</tr>
<tr>
<td>Manganese</td>
<td>2%</td>
</tr>
<tr>
<td>Cadmium</td>
<td>80%</td>
</tr>
<tr>
<td>Lead</td>
<td>70%</td>
</tr>
</tbody>
</table>
Directive related to the spent battery handling
DIRECTIVE 2006/66/EC

Purpose: to reduce the quantity of spent batteries and accumulators disposed in an inadequate way, setting European targets for collection and recycling

September 26, 2008

– Applied to all batteries and accumulators;
– Incineration and landfilling strictly prohibited.

Minimum collection rates:
– 25% by 26 September 2012;
– 45% by 26 September 2016.

Directive implemented in Swedish directive - SFS 2008:834
Producer Obligations
Article 12 – Treatment and Recycling

- By 26 September 2009 producers to provide for treatment and recycling using best available techniques (BAT).
- Batteries and accumulators collected with WEEE must be removed.
- Specified recycling efficiencies to be achieved by 26 September 2011:
  - lead-acid batteries and accumulators, including lead recycling – 65%
  - nickel-cadmium batteries and accumulators, including cadmium recycling – 75%
  - other waste batteries and accumulators – 50%.
Collection system

"Only collected batteries can be recycled! "
## Collection systems in Europe

<table>
<thead>
<tr>
<th>Country</th>
<th>Collection system</th>
</tr>
</thead>
<tbody>
<tr>
<td>France</td>
<td>SCRELEC, COREPILE</td>
</tr>
<tr>
<td>Finland</td>
<td>RECSER Oy</td>
</tr>
<tr>
<td>Greece</td>
<td>AFIS</td>
</tr>
<tr>
<td>Denmark</td>
<td>BatteriForeningen</td>
</tr>
<tr>
<td>Netherland</td>
<td>STIBAT</td>
</tr>
<tr>
<td>Ireland</td>
<td>WEEE Ireland, ERP</td>
</tr>
<tr>
<td>Hungary</td>
<td>RE`LEM</td>
</tr>
<tr>
<td>Germany</td>
<td>GRS</td>
</tr>
<tr>
<td>Norway</td>
<td>As Batteriretur</td>
</tr>
<tr>
<td>Poland</td>
<td>REBA</td>
</tr>
<tr>
<td>Portugal</td>
<td>ECOPILHAS</td>
</tr>
<tr>
<td>Austria</td>
<td>UHF, ERA, EVA, ERP, CCR</td>
</tr>
<tr>
<td>Switzerland</td>
<td>Inobat</td>
</tr>
<tr>
<td>Sweden</td>
<td>El-Kretsen (Renova)</td>
</tr>
<tr>
<td>UK</td>
<td>G&amp;P</td>
</tr>
<tr>
<td>Slovakia</td>
<td>INSA</td>
</tr>
<tr>
<td>Norway</td>
<td>Rebatt</td>
</tr>
<tr>
<td>Belgium</td>
<td>BEBAT</td>
</tr>
<tr>
<td>Czech republic</td>
<td>ECOBAT</td>
</tr>
</tbody>
</table>
Sorting

“No recycling process can handle all types of battery chemistries, so sorting is crucial in maintaining product quality. Once waste batteries have been sorted, several different recycling processes exist.”
1. Manual sorting
2. Automatic sorting
X-Tract sorting principle (TITECH)
Recycling processes of spent batteries

- Mechanical pre-treatment and separation
- Pyrometallurgy
- Hydrometallurgy
Pre-treatment and separation of the batteries

- Dismantling
- Crushing
- Milling
- Separation
Pre-treatment:
- Crushing
- Milling
- Disintegration

Separation: (based on different physical properties)
- Sieving
- Magnetic separation
- Electrodynamic separation
- Air separation
- Electrostatic separation, etc.
Zn-C and Alkaline batteries recycling
Pyrometallurgical Processes

- At 900 °C to separate metals by volatilization.
- Iron and manganese remain in liquid form.
- Vaporized products include:
  - organics,
  - mercury,
  - potassium,
  - carbon, and
  - zinc.

- Pyrometallurgical recycling processes suitable for recycling alkaline batteries are
  - Batrec’s process in Switzerland,
  - Citron’s process in France, and
  - Valdi’s process also in France.
Batrec’s process

1. Manually sorting.
2. Heating in the furnace at temperatures up to $700^\circ$ C.
3. Mercury vaporises - condensation and recovery via distillation.
4. Smelting in the induction furnace with a reducing environment at $1500^\circ$ C.

The high temperature causes the manganese to combine with the remaining iron components, producing **ferromanganese**.

Zinc is completely vaporized, and condensed for recovery.
By dissolving the electrode powders in an acidic solution.

After this, metals can be separated from one another by altering pH of the solution, adding reaction agents to precipitate metallic salts, electrolysis, and liquid-liquid extraction steps.

Several companies developed hydrometallurgical processes; these include

Batenus,
Recupyl,
Recyctec, and
Revatech.
Lead batteries
Collection

- Collection level to 100% 2009, 98% 2010, 100% 2011 and 96% 2012 in Sweden.

- The lead acid industry has through the company BlyBatteriRetur created a nationwide and very cost efficient system, which meets all the requirements of the law.

- BlyBatteriRetur is owned by the more important battery companies in Sweden as well as by the trade organization SWEBATT.
Lead-acid battery construction

- Positive plate pack
- Microporous separator
- Positive cell connector
- Negative cell connection
- Grid plate
- Negative pole
- Negative plate
- Positive plate
- Valve
- Casing
- Terminal
### Material composition of lead batteries

**Lead = 2500 $/ton**

<table>
<thead>
<tr>
<th>Component</th>
<th>[wt.-%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lead (alloy) components (grid, poles)</td>
<td>25 - 30</td>
</tr>
<tr>
<td>Electrode paste (fine particles of Lead oxide and Lead sulphate)</td>
<td>35 - 45</td>
</tr>
<tr>
<td>Sulphuric acid (10 - 20 % H2SO4)</td>
<td>10 - 15</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>5 - 8</td>
</tr>
<tr>
<td>Other plastics (PVC, PE, etc.)</td>
<td>4 - 7</td>
</tr>
<tr>
<td>Ebonite</td>
<td>1 - 3</td>
</tr>
<tr>
<td>Others materials (glass, etc.)</td>
<td>&lt; 0.5</td>
</tr>
</tbody>
</table>
Recycling process:

1. **Batteries breaking:**
   * batteries are broken in a hammer mill or another type of crushing machine.

2. **Separation by different density (in the water)**
   * The pieces from the breaking process are placed in a tank, where the dissimilar densities of the materials cause some to sink (lead), some to float (hard rubber and plastic) and liquids to go into solution (battery acid).

3. **The acid is neutralized.**

\[
\begin{align*}
H_2SO_4 + 2NaOH & \rightarrow Na_2SO_4 + 2H_2O & (1) \\
PbSO_4 + 2NaOH & \rightarrow Na_2SO_4 + PbO + H_2O & (2)
\end{align*}
\]
4. Lead reduction:

- The battery scrap obtained from the breaking process is a mixture of several substances: metallic lead, lead oxide, lead sulphate and other metals such as calcium, copper, antimony, arsenic, tin and sometimes silver.

- In order to isolate the metallic lead from this mixture, these materials are charged into a furnace together with appropriate fluxes & reductants, drosses, returning slags and process dusts for smelting.

- Off-gases from the smelting furnace are filtered and the dust collected is returned to the furnace.

- The metal tapped from the kiln is transferred to refining kettles and processed to produce commercial quality lead.

5. Lead refining:

- As a smelting plant stops at the stage of the reduction plant, it will produce what is known as hard or antimonial lead.

- If the plant wants to produce soft lead, other metals like copper, antimony, arsenic and tin have to be removed.

- The refining process is applied in several steps in kettles with addition of specific agents.

- After this process the soft lead can be poured into moulds called “ingots”.

- These ingots are sold on the local or international market.
Li-ion batteries
Li-ion batteries and accumulators

Portable lithium batteries are used in: cell phones, computers, laptops, cameras, portable DVD, mp3 – mp4 players, memory sticks, etc.

Until 2020 – 12 mil. of electric cars will be produced (car battery is approximately 150kg!).

Secondary raw material - Co, Li, Cu, Al, Ni,...
(primary raw material contains 0.13 – 5% of Co)
Chemical composition of LiB

- Al (15-25%)
- Cu foil (5-15%)
- LiCoO₂ (25-45%)
- LiPF₆ (1-5%)
- graphite (10-30%)
- steel, Ni and inert polymer

- diethyl carbonate (1–10%)
- ethylene carbonate (1–10%)
- methyl ethyl carbonate (1–10%)
- polyvinylidene fluoride (0.5–2%)
Lithium accumulators material characterization

- External case
- Separator
- Current collectors
- Black mass
- Printed circuit boards
RECYCLING

Mechanical pre-treatment
- Steel
- Plastic
- Al cover
- Electrolyte
- Al/Cu foils

Pyrometallurgical treatment
- Co
- Ni
- Cu
- Fe
- Electrolyte and polymers

Hydrometallurgical treatment
- Co
- Ni
- Cu
- Fe
- Electrolyte
A couple of general non-technical questions

Dedicated or General recycling

Local or Centralised recycling
Dedicated recycling

+ Energy efficient
+ High purities
+ Can be designe to minimise secondary waste
- A large number of processes / competences needed
- Often complicated and sensitive systems
- Require a large, uniform waste-stream

General recycling

+ Simple traditional methods (bash and burn)
+ Robust processes with high throughput
- Difficult materials separation issues (sorting)
- Creates seconday waste which may be difficult to handle
- Often require selective pretreatment e.g. freon in fridges
"Local" recycling

+ Energy efficient (few transports)
+ Special design for connection directly to manufacturing
+ Can treat manufacturing waste + product recycling
- A large number of process places / competences
- Must be robust to withstand lack of competence

Centralised recycling

+ Coordination profits (personnel competences etc.)
+ Profit margins
+ Higher turnover
- Transports and logistics
- Difficult to optimise when the feed changes
Final thoughts

There are too many different shapes and chemistries today to ensure an efficient general recycling process.

There is a need to develop batteries with recycling in mind.

If a battery is designed to be recycled than the need to come up with new chemical solutions will be less pressing.
Thank you for your attention!

Questions?