Valorization of Spent Lithium Ion Accumulators

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2006 European Battery Directive

Mandatory collection rate of used portable batteries

- 25% on September 2012
- 45% on September 2016

Mandatory levels of metal recovery (September 2011)

- 65% (w/w) for Lead accumulators
- 75% (w/w) for Ni-Cd
- 50% (w/w) for all other kinds of batteries
Li-ion accumulators

Li-ion accumulators are made up of carbon on copper as anode and by LiCoO$_2$ (LiNiO$_2$, LiMnO$_2$ and based Fe or Cu) on Aluminum foil as cathode.
Stagnation of the quantities of used portable batteries recycled in 2008 (only +1% of collection with respect to 2007, while during the same period, the quantity of used rechargeable batteries processed has increased of +44%)

In 2008 the global quantity of used portable batteries collected in Europe is 35,000 tons (27,600 tons by EBRA members + 8,000 tons by non-Ebra members)

Compared to the 190,000 tons of portable batteries marketed each year in Europe, 2008 collection rate is 18.5%

### Collection rate

<table>
<thead>
<tr>
<th>Type of batteries</th>
<th>2007</th>
<th>2008</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkaline, Zinc-Carbon, Zinc-air</td>
<td>26,840</td>
<td>26,553</td>
<td>-1.4%</td>
</tr>
<tr>
<td>Lithium Primary</td>
<td>306</td>
<td>212</td>
<td>-31%</td>
</tr>
<tr>
<td>Nickel-cadmium portable (Sealed)</td>
<td>2,688</td>
<td>2,870</td>
<td>+6.7%</td>
</tr>
<tr>
<td>Nickel-Metal hydride</td>
<td>611</td>
<td>904</td>
<td>+48%</td>
</tr>
<tr>
<td>Lithium-ion</td>
<td>458</td>
<td>1919</td>
<td>+318%</td>
</tr>
<tr>
<td>Button Cells</td>
<td>70</td>
<td>163</td>
<td>+130%</td>
</tr>
<tr>
<td>Total portable batteries</td>
<td>31,078</td>
<td>32,621</td>
<td>+5%</td>
</tr>
<tr>
<td>Nickel-Cadmium Industrial</td>
<td>4,404</td>
<td>3,641</td>
<td>-13%</td>
</tr>
</tbody>
</table>
High-Tech Recycling Centre (HTR) was founded in 2007 and gets together several Italian Universities with the common goal of developing innovative processes for the valorization, recycling and treatment of wastes.

Sapienza University of Rome
University of l’Aquila
University of Marche

Block diagram for recycling

Li-ion accumulators $\rightarrow$ Pre-treatments $\rightarrow$ Paper, plastic, iron-steel and copper

Electrodic material $\downarrow$ Leaching

Leach liquor $\downarrow$ Purification

Li-Co solution $\downarrow$ Recovery $\rightarrow$ Li and Co products
Leaching

Sulphuric or hydrochloric acid were used as leachant:

\[4\text{LiCoO}_2(s) + 6\text{H}_2\text{SO}_4 \rightarrow 4\text{CoSO}_4(aq) + 2\text{Li}_2\text{SO}_4(aq) + 6\text{H}_2\text{O} + \text{O}_2(g)\]

\[4\text{LiCoO}_2(s) + 12\text{HCl} \rightarrow 4\text{CoCl}_2(aq) + 4\text{LiCl}(aq) + 6\text{H}_2\text{O} + \text{O}_2(g)\]

\(\text{H}_2\text{SO}_4\) required a reducing agent such as \(\text{H}_2\text{O}_2\) to quantitatively extract the cobalt:

\[2\text{LiCoO}_2 + 3\text{H}_2\text{SO}_4 + \text{H}_2\text{O}_2 \rightarrow \text{Li}_2\text{SO}_4 + 2\text{CoSO}_4 + \text{O}_2 + 4\text{H}_2\text{O}\]

**INVESTIGATED VARIABLES**
- acid stoichiometry: (1-2 g/g)
- temperature: \(\text{T}_{\text{env}}\) 70 - 90°C
- \(\text{H}_2\text{O}_2\): +50%, +100%

**Leaching**

Significant effects of investigated factors were determined by analysis of variance.

**HCl**

Significant effect of temperature rise from 25 to 70°C, while the increase of acid/solid ratio in the investigated range (from 1 to 2 g of acid per g of solid sample) does not affect significantly the extraction yields of metals.

**Optimised conditions**: 70°C; 1.0 g acid per g of solid sample

**\(\text{H}_2\text{SO}_4\) + reducing agent**

Significant positive effects of both temperature and acid concentration, while the increase of reducing agent in the investigated range does not affect significantly the extraction yields of metals.

**Optimised conditions**: 80°C; 2g acid per g of solid; 50% stoichiometric excess of reducing agent
Solid concentration with sulphuric acid

Increasing the solid concentration in the mixture
a. Weak decrease of metal extractions
b. Reduction of equipment costs in a bigger scale

Purification by Precipitation

leach-liquor (S/L 1:5)
50 g/l of Co
10 g/l of Li
7 g/l of Al
5 g/l of Ni
2 g/l of Fe
3 g/l of Cu
2 g/l of Mn

Primary purification
Chemical precipitation

• Quantitative removal of (Al and Fe)
• Partial removal of Copper
• Ni and Co can not be separated by precipitation for a simple pH effect
**PRODUCTS**

### COBALT RECOVERY

Sodium carbonate addition to purified leach liquor samples determined the quantitative precipitation (>95%) of Co as carbonate (82% purity). This precipitation is not selective because also Ni (4-5% w/w) and Mn (1% w/w) precipitate as carbonates along with Co (35-36% w/w).

### LITHIUM RECOVERY

Li was recovered as carbonate: after Co recovery 80-90% of water was evaporated, Li$_2$CO$_3$ crystals formed with a final yield >80% (purity 98% w/w).

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**Diagram:**

- **COBALT RECOVERY**
  - Waste
  - Leaching
  - Leach liquor
  - Purification I
  - Recovery of Products
  - CoCO$_3$ (36-37% Co w/w) → Li$_2$CO$_3$ (98%) (3.5 $/kg)

- **SIMULATION**
  - Experimental results
  - Design of equipment
  - Economical parameters
Economical profits is always proportional to the amount of treated waste. This process becomes suitable selling the cobalt carbonate at least for 10$/kg.

Selling the product for 10 $/kg, the minimum amount of powder we must treat to have a reasonable profit is 175 tonnes/year (350 t/y of Spent LIA).

Economical profits is always proportional to the amount of treated waste.

**CONCLUSIONS**

1. According to EU guidelines lithium ion accumulators must be recycled.
2. The best experimental condition to extract Co and Li from the electrocic powder was identified (2 g H₂SO₄/g powder, 80°C, + 50% H₂O₂).
3. Leach liquor purification can be performed by precipitation.
4. 80% of lithium was recovered as carbonate with a purity of 98%.
5. 95% of cobalt was recovered as a carbonate with a content of cobalt of 36-37%.
6. The process would become economically suitable selling the Co product at least for 10 $/kg and the minimum amount of waste which must be treated to have a suitable process is 350 t/y.
THANKS FOR YOUR ATTENTION