Abstract:
The present invention concerns a process for the recovery of metals and of heat from spent rechargeable batteries, in particular from spent Li-ion batteries containing relatively low amounts of cobalt. It has in particular been found that such cobalt-depleted Li-ion batteries can be processed on a copper smelter by: feeding a useful charge and slag formers to the smelter; adding heating and reducing agents; whereby at least part of the heating and/or reducing agents is replaced by Li-ion batteries containing one or more of metallic Fe, metallic Al, and carbon. Using spent LFP or LMO batteries as a feed on the Cu smelter, the production rate of Cu blister is increased, while the energy consumption from fossil sources is decreased.
Process for recycling Li-ion batteries

The present invention concerns a process for the recovery of metals and of heat from spent rechargeable batteries, in particular from spent Li-ion batteries containing relatively low amounts of cobalt.

In Europe, the societal need for metals recycling is being translated into a number of so-called directives. Directive 2006/66/EC of the European Parliament and of the Council of 6 September 2006 relates to batteries and accumulators, and to waste batteries and accumulators, and regulates their manufacture and disposal in the EU (European Union). It entered into force on 26 September 2006.

Pursuant to this directive, EU Commission Regulation No. 493/2012 of 11 June 2012 lays down detailed rules regarding the calculation of recycling efficiencies. This Regulation shall apply to the recycling processes carried out in respect of waste batteries and accumulators from 1 January 2014. The recycling targets are 75% by average weight for nickel-cadmium batteries, 65% for lead acid batteries, and 50% for others.

Several families of battery recycling processes are known. Most of these include a mechanical pre-treatment, typically an initial shredding step, followed by physical separations. Fractions having distinct compositions are obtained: dedicated chemical processes are then applied to each fraction for the further separation and refining of the contents.

Shredding and physical separations are all but straightforward when dealing with Li-ion batteries. The lithium in the battery will react violently with air moisture and ignite the electrolyte and separators. Moreover, recycled batteries are not necessarily fully discharged: shredding will provoke short-circuits with high currents and local heating as a result. This situation may also induce fires. Cryogenic, vacuum, or inert atmosphere techniques mitigate the risks, but complicate the pre-treatment considerably.

Smelting processes solve this problem by allowing a furnace to be directly fed with complete cells or even with complete cell assemblies or modules, as long as the mass and dimensions of the lumps permit reasonable handling. However, the lack of pre-treatment transfers the burden of the separation and refining to chemical processes entirely.

Such routes are known from e.g. EP1589121 and EP2480697. They aim at the recovery of the most valuable metals, notably nickel and cobalt. Strongly reducing conditions and high process temperatures are however necessary to achieve this goal.

In recent years, the demand for rechargeable batteries as mobile energy sources has constantly increased. Consequently, the market share of Li-ion has been growing steadily, and several specific Li-ion battery technologies have been developed to fulfill the diversifying technical needs. Initially, most Li-ion rechargeable batteries made use of cathode material based on LCO (Lithium-Cobalt-Oxide), containing respectable amounts of cobalt. Nowadays, other chemistries are commonplace, such as LFP (Lithium-Iron-Phosphate) and LMO (Lithium-Manganese-Oxide), which contain little or no cobalt. LFP and LMO batteries are in high demand for electric power tools and E-bikes, for example. Electrical vehicles often take advantage of NMC (Nickel-Manganese-Cobalt) batteries, wherein the amount of cobalt is limited. The reduction or elimination of cobalt entails technical advantages, reduces the costs, and minimizes materials costs fluctuations that are typical with higher cobalt cathode compositions.
Table 1 shows typical composition ranges of the different types of battery cells in common use. The LMO and LPF chemistries show low low-cobalt contents consistently.

<table>
<thead>
<tr>
<th>Chemistry</th>
<th>Li</th>
<th>Ni</th>
<th>Mn</th>
<th>Co</th>
<th>Fe</th>
<th>Cu</th>
<th>Al</th>
</tr>
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<tbody>
<tr>
<td>LCO</td>
<td>1-2</td>
<td>2-8</td>
<td>0-2</td>
<td>10-15</td>
<td>10-15</td>
<td>5-10</td>
<td>5-10</td>
</tr>
<tr>
<td>LMO</td>
<td>1-2</td>
<td>2-8</td>
<td>10-20</td>
<td>0-3</td>
<td>0-5</td>
<td>10-20</td>
<td>10-20</td>
</tr>
<tr>
<td>NMC</td>
<td>1-2</td>
<td>2-8</td>
<td>2-8</td>
<td>0-10</td>
<td>0-10</td>
<td>10-20</td>
<td>10-20</td>
</tr>
<tr>
<td>LFP</td>
<td>1-2</td>
<td>0-1</td>
<td>0-1</td>
<td>0-1</td>
<td>5-20</td>
<td>10-30</td>
<td>5-15</td>
</tr>
</tbody>
</table>

Achieving high recovery yields for cobalt is therefore not as crucial as it used to be, at least when considering a feed comprising low-cobalt Li-ion batteries mainly. In view of this, a smelter process wherein cobalt is oxidized, and thus reports to the slag without being recovered, has become economically viable.

While a dedicated smelting process could be considered, it has now been found that a relatively standard copper smelting process is particularly well suited for treating low-cobalt Li-ion batteries. The batteries can be added in addition to the normal copper-bearing feed.

It has in particular been found that such cobalt-depleted Li-ion batteries can be processed on a copper smelter by:
- feeding a useful charge and slag formers to the smelter;
- adding heating and reducing agents;
whereby at least part of the heating and/or reducing agents is replaced by Li-ion batteries containing one or more of metallic Fe, metallic Al, and carbon.

In Li-ion rechargeable batteries, the foil supporting the anode is normally made of metallic Cu, while the foil supporting the cathode is made of metallic Al. Carbon is the typical anode active material; the cathode active
material contains one or more of Ni, Mn, Co, and Fe. The casing of the batteries normally contains metallic Al, Fe and/or plastics.

Thanks to their particular composition, rechargeable Li-ion batteries used as an additional feed on top of the standard feed on a Cu smelter can increase the production rate of Cu blister significantly, while considerably lowering the need for fuel. It is here assumed that the fuel needs are compensated by the metallic aluminum, carbon and the plastics present in the battery feed.

The process should preferably remain within commonly accepted boundaries by adjusting the slag formers, and $\text{SiO}_2$ in particular, to comply with $0.5 < \text{SiO}_2 / \text{Fe} < 2.5$ and with $\text{Al}_2\text{O}_3 < 10\%$.

For environmental reasons, it is advisable to aim for a slag wherein cobalt is below 0.1%. This can be achieved by limiting the amount of batteries in the useful charge and/or increasing the proportion of low-cobalt batteries. In any case, it is preferred to feed a major part of low-cobalt batteries. By "low-cobalt" is meant that batteries containing 3% of cobalt or less. By "major part" is meant more than 50% of the total of the batteries present in the useful charge (i.e. excluding flux).

The furnace should be equipped with a feeding system capable of handling relatively large aggregates or lumps having a dimension of at least 1 cm. Also, adequate gas cleaning equipment has to be provided, as Li-ion batteries contain large amounts of halogens, and of fluorine in particular. Such provisions are known and relatively common in copper smelters.
Example 1: Reference charge without batteries

A typical charge for the smelter is shown in Table 2 below.

Table 2: Reference charge of Cu smelter (wt.%)  

<table>
<thead>
<tr>
<th>Feed rate (t/h)</th>
<th>Li</th>
<th>S</th>
<th>Ni</th>
<th>Mn</th>
<th>Co</th>
<th>Fe</th>
<th>Cu</th>
<th>Al</th>
<th>Al₂O₃</th>
<th>SiO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 (Reference)</td>
<td>-</td>
<td>18</td>
<td>0.6</td>
<td>-</td>
<td>-</td>
<td>20</td>
<td>25</td>
<td>-</td>
<td>1</td>
<td>15</td>
</tr>
<tr>
<td>23.2 (Flux)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>100</td>
</tr>
</tbody>
</table>

The balance of the reference charge (20%) is moisture. A S₉O₂ / Fe ratio 2.2 is maintained by addition of silica (23.2 ton/h), while Al₂O₃ is kept below 6% in the slag. At a feed rate of 100 ton/h, 18% of this feed is converted to Cu blister, 60% to slag, with the gases (mainly SO₂) closing the material balance.

The fuel consumption amounts to 3000 l/h, together with 18000 Nm³/h oxygen.

Example 2: Reference charge including LFP batteries

A charge including LFP batteries and additional flux is shown reported in Table 3 below.

Table 3: Reference charge including LFP batteries and additional flux (wt.%)  

<table>
<thead>
<tr>
<th>Feed rate (t/h)</th>
<th>Li</th>
<th>S</th>
<th>Ni</th>
<th>Mn</th>
<th>Co</th>
<th>Fe</th>
<th>Cu</th>
<th>Al</th>
<th>Al₂O₃</th>
<th>SiO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 (Reference)</td>
<td>-</td>
<td>18</td>
<td>0.6</td>
<td>-</td>
<td>-</td>
<td>20</td>
<td>25</td>
<td>-</td>
<td>1</td>
<td>15</td>
</tr>
<tr>
<td>17.6 (Batteries)</td>
<td>1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>15</td>
<td>25</td>
<td>10</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>29.0 (Flux)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>100</td>
</tr>
</tbody>
</table>

A S₉O₂ / Fe ratio of 2.2 is maintained by adding of 5.8 t/h of S₉O₂, with respect to the reference case. Al₂O₃ is kept below 6% in the slag by limiting the amount of added LFP batteries to 17.6 t/h. This corresponds to a yearly capacity of about 60000 tons of batteries, which is appreciable in view of the quantities of spent batteries of this type presently available on the market.
Using spent batteries as a feed on the Cu smelter, the production rate of Cu blister is thus increased with more than 20%, while hazardous waste is being recycled. Of course, this is dependent upon the relative amounts of Cu present in the reference smelter charge and in the spent batteries.

Due to the high calorific value of the LFP battery feed and to the battery-related Cu being present as metal instead of as oxidized species, the fuel consumption can be decreased from 3000 l/h to 2000 l/h, while the oxygen consumptions rises from 18000 Nm$^3$/h to 20000 Nm$^3$/h to maintain the furnace heat balance. This is a reduction of more than 30% of the energy consumption from fossil sources.
Claims

1. Process for the recovery of enthalpy and metals from Li-ion batteries on a copper smelter, comprising the steps of:
   - feeding a useful charge and slag formers to the smelter;
   - adding heating and reducing agents;
   characterized in that at least part of the heating and/or reducing agents is replaced by Li-ion batteries containing one or more of metallic Fe, metallic Al, and carbon.

2. Process according to claim 1, wherein the slag formers comprise $\text{SiO}_2$ in an amount sufficient to comply with $0.5 < \frac{\text{SiO}_2}{\text{Fe}} < 2.5$ and with $\text{Al}_2\text{O}_3 < 10$ wt.% in the slag.

3. Process according to claims 1 or 2, wherein the major part of the Li-ion batteries contain 3 wt.% of Co or less.

4. Process according to claim 3, wherein an amount of Co in the slag of less than 0.1 wt.% is obtained by feeding a major part of low-cobalt batteries.
## INTERNATIONAL SEARCH REPORT

**PCT/EP2014/075500**

### A. CLASSIFICATION OF SUBJECT MATTER

**INV. C22B7/00 C22B7/04**

**ADD.**

According to International Patent Classification (IPC) etc, both national classification and IPC

### B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C22B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic database consulted during the international search (name of database and, where practicable, search terms used)

EPO-Internal, WPI Data

### C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents:

- **A** document defining the general state of the art which is not considered to be of particular relevance
- **E** earlier application or patent but published on or after the international filing date
- **L** document which may throw doubts on priority claim(s) on which is cited to establish the publication date of another citation or other special reason (as specified)
- **O** document referring to an oral disclosure, use, exhibition or other means
- **P** document published prior to the international filing date but later than the priority date claimed

- **T** later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- **X** document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- **Y** document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- **Z** document member of the same patent family

Date of the actual completion of the international search

17 February 2015

Date of mailing of the international search report

27/02/2015

Name and mailing address of the ISA/

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NL-2280 HV Rijswijk
Tel. (+31-70) 340-2040; Fax. (+31-70) 340-3016

Authorized officer

Swiatek, Ryszard
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<td>EP 1589121</td>
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