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Valorisation of battery recycling slags

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Abstract

Portable electronics are more and more common in everyday life. E-mobility is starting to kick-off. In both these applications, intensive use is made of rechargeable batteries. European legislation on the other hand imposes strict regulations on collection and recycling of these batteries at their end-of-life. In recent years, Umicore has developed a closed-loop flowsheet for the production and recycling of battery materials. In this paper, the basic building blocks of this flowsheet are discussed with particular attention to the valorisation of the produced slag phase in construction applications and to lithium recovery.

Introduction

In everyday life, batteries are everywhere. Cellular phones, PDA's, MP3 players, digital camera's, laptops, and, more and more, hybrid (HEV) and electrical (EV) vehicles make our life more comfortable because of instant power provided by rechargeable batteries. This trend is only expected to increase, as visualised in Figure 1, which shows the evolution of the demand of power via Li-ion batteries in several applications.

This evolution, however, leads to a pressing question: what will we do with these high-tech appliances, and more particular with the batteries, at their end-of-life? Especially the (H)EV marked is expected to boom, leading to vast amounts of waste material, as shown in Figure 2.

Policy makers have realised that landfilling this hazardous waste can hardly be called a sustainable solution. Therefore, Directives have been issued at the EU level to regulate the end-of-life of such problematic waste streams. The WEEE directive⁴ states that batteries have to be removed from waste electrical and electronic equipment and be treated separately. The Battery Directive,⁵ dealing with all

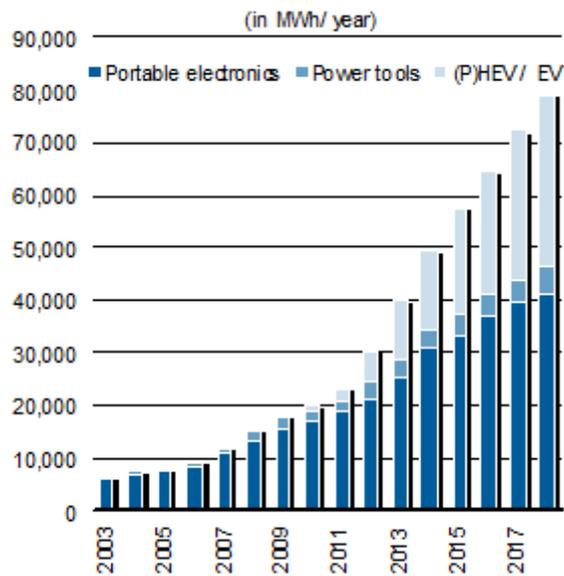


Figure 1: Power demand of Li-ion batteries¹

batteries and accumulators or rechargeable batteries, imposes strict collection targets of 25% by 2012 and 45% by 2016, while demanding recycling efficiencies of more than 50%. From this it is clear that the stakes are high, and the challenges daunting.

Umicore, being one of the market leaders in advanced products for rechargeable batteries, made the strategic choice to develop a process to recycle end-of-life batteries and to produce new battery materials from this waste, thus effectively

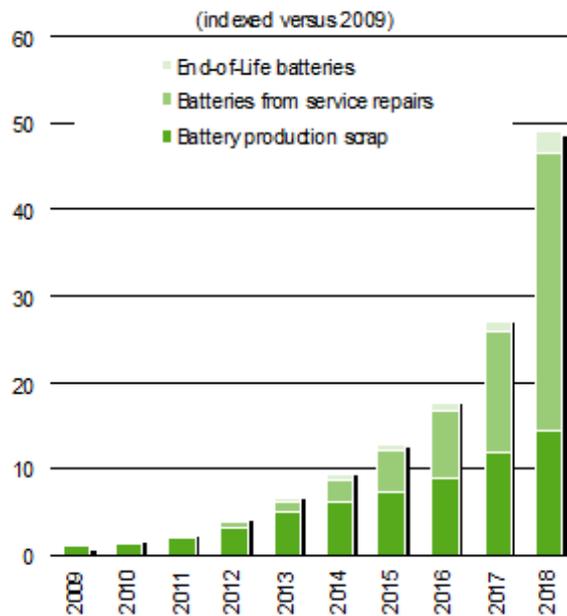


Figure 2: Potential recyclable (H)EV battery material²

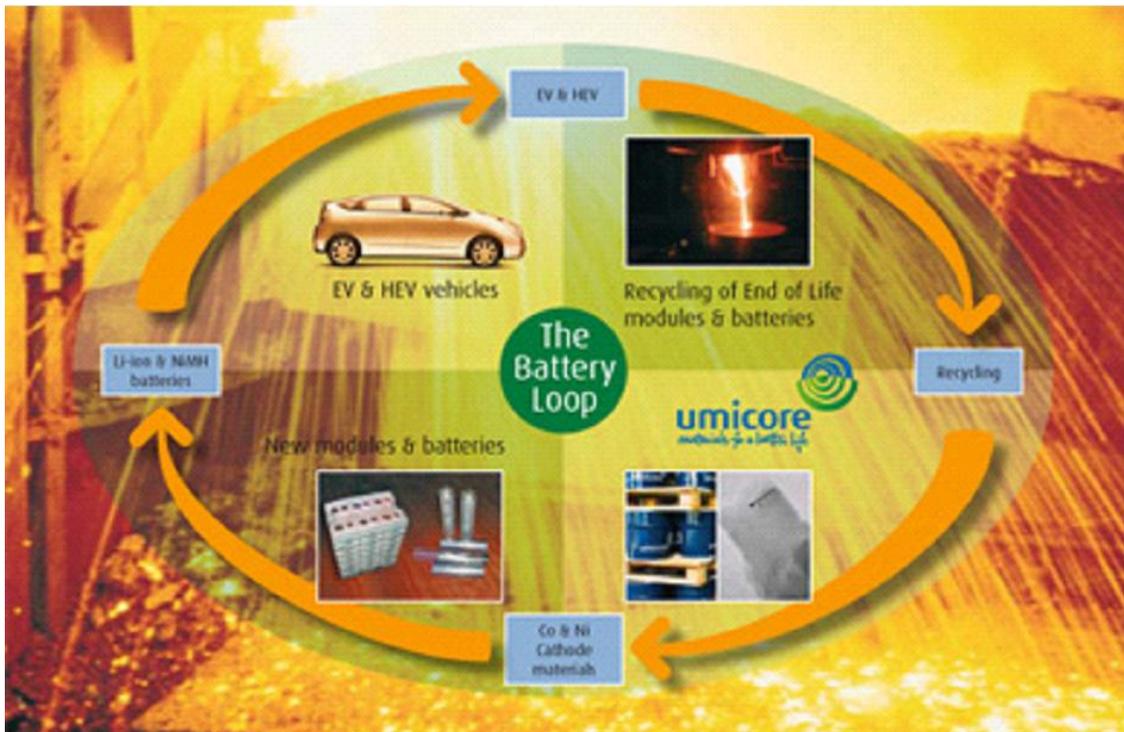


Figure 3: The closed loop solution for rechargeable batteries³

closing the materials loop from battery to battery, as shown in Figure 3. On November 16th, 2009 Umicore sent out a press release announcing an investment of 25 M€ in the construction of an industrial scale recycling facility for end-of-life rechargeable batteries in Hoboken, Belgium. In what follows, the main components of Umicore’s battery loop will be described, with particular focus on the valorisation of all produced streams and special attention for the recovery of Li from the slag phase.

Umicore’s battery recycling flowsheet³

Figure 4 shows a schematic overview of the flowsheet for the recycling and production of battery materials. The total closed loop consists of five steps:

- step 0: collection and reception of batteries (worldwide and Hoboken, Belgium);
- step 1: smelting and energy valorisation (Hoboken, Belgium);
- step 2: refining and purification of metals (Olen, Belgium);
- step 3: oxidation of cobalt chloride into cobalt oxide (Olen, Belgium);
- step 4: production of lithium metal oxide for new batteries (South Korea).

In what follows, a number of these process steps will be described in more detail.

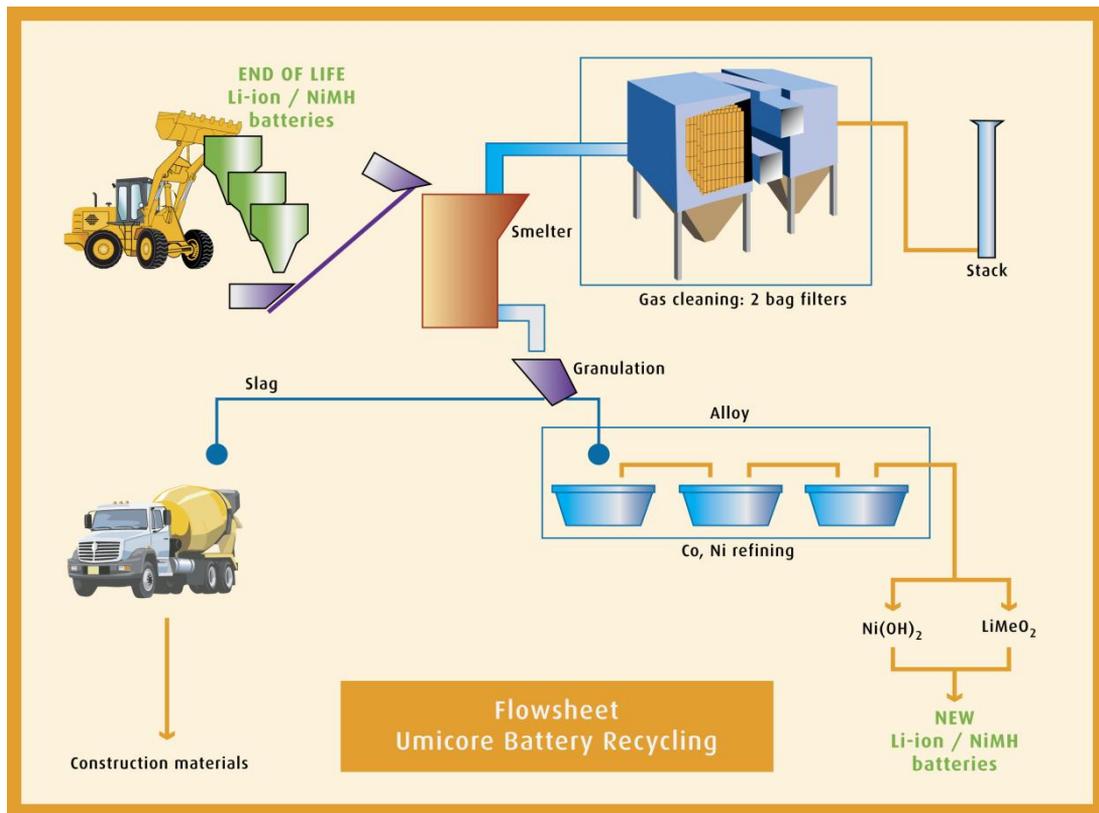


Figure 4: Umicore battery recycling flowsheet

Step 1: smelting and energetic valorisation

No pre-treatment is necessary to feed the batteries into the furnace. Only in the case of large HEV batteries some dismantling is needed for mechanical reasons. The batteries with their plastic housing/can are directly fed into the operation furnace with the objective to evaporate the electrolyte (if present), melt all metals, recover all caloric capacity of plastics and other inorganic compounds (other than graphite) and use the graphite of the electrode as a reducing agent in the reaction zone of the furnace to reduce all metal oxides into their metallic form.

Three phases are formed in this process, namely a metal phase, capturing the valuable metals such as cobalt, copper, nickel and iron, a slag phase based on lime, alumina and lithium, and a gas phase. The metal phase is sent to the next steps of the flowsheet to valorise the metal content. The slag phase can be used directly in construction applications or can be processed further for lithium valorisation, as will be discussed in a subsequent section. The gas phase is processed in a state-of-the-art gas cleaning system, avoiding dioxin and furan formation, and capturing any halogen or other hazardous substances.

Step 2: refining and purification of metals

This operation has already been existing within Umicore for several decades. The alloy produced during smelting is leached in sulphuric acid. Via several purification steps, a separation of the main metals is achieved and CoCl_2 is produced together with a solution of NiSO_4 . The NiSO_4 is further purified via solvent extraction. After a crystallisation step, the NiSO_4 crystals can be further transformed into spherical Ni(OH)_2 for potential application in NiMH batteries, thus closing the battery loop for this type of batteries. The CoCl_2 solution is used in the following step.

Step 3 & 4: oxidation to cobalt oxide and production of lithium metal oxide

The pure CoCl_2 is oxidised in a closely controlled, dedicated furnace to produce high quality cobalt oxide. This oxide is processed with Li_2CO_3 to finally produce LiCoO_2 and thus closing the loop for the Li-ion batteries.

Slag valorisation

Slag properties

The slag produced during the recycling of rechargeable batteries contains the main components of construction materials, mainly calcium oxide (CaO), aluminum oxide (Al_2O_3), silicon dioxide (SiO_2), minor amounts of iron oxide (Fe_2O_3), lithium oxide (Li_2O) and manganese oxide (MnO), which are substitutes for the primary limestone, clay, sand, bauxite, ferromanganese, etc. The particle size ranges between 0-4 mm and 4-32 mm.

Regulation

As Umicore's Battery Recycling facility is located in Belgium, the produced slag materials are subjected to the VLAREA standards which are defined by the local Flemish authority OVAM. OVAM stands for "*Openbare Afvalstoffenmaatschappij voor het Vlaams Gewest*" (E: Public Waste Agency of Flanders) and is responsible for waste management and soil remediation in Flanders. The slag also fulfils the requirements under the REACH, CE marking, waste and construction directives.

As the feed material is the battery, the presence of some critical materials in the slag may cause adverse effects on organisms, human health and environment. Therefore, the leaching properties of the slag are followed closely by considering the requirements of REACH and the Directives.

Construction applications

The produced slag resulting from the recycling of rechargeable batteries is suitable as aggregate, cement raw materials or filling material for concrete applications. Recently the slag has been used as a filling material in an industrial facility construction in Sweden because of the high quality and leaching properties. Besides using as a filling material, the suitability of the slag to be used as an aggregate is analysed according to EN 12620:2002+A1 (Aggregates for concrete). The mechanical properties are given in Table 1.

Table 1: Suitability of the “slag” as an aggregate

Tests	EN Standard	Slag (Fine & Coarse aggregate)
Free CaO (%)	1744-1 § 18 (1998)	0.22
Free MgO (%)	1744-1 § 18 (1998)	<1%
Los Angeles Coefficient (La)	1097-2 (1998)	24
Micro Deval Coefficient (MD)	1097-1 (1996)	10

The Los Angeles test analyses the resistance to fragmentation of aggregate and the Micro-Deval test checks the resistance to wear of aggregate. Test results are helpful in evaluating the suitability of fine/coarse aggregates subject to fragmentation, weathering and abrasive action. As mentioned on EN 12620:2002+A1; LA15 or LA20 is generally only required in special cases. If LA is less than 30 (LA30), it is considered strong enough to be used in coating & road surface treatments. Aggregates are suitable to be used in concrete when $MD \leq 20$.

These results show the suitability of the slag in construction industry. Nevertheless, the research on the improvement of the slag is continuing, in order to be able to extend the application possibilities.

CO₂ neutrality

Nearly 5% of global man-made CO₂ emissions are produced by cement manufacturers. Therefore, the construction industry is always looking for new improvements on the manufacturing processes. In the report published by CEMBUREAU (The European Cement Association), some alternative ways are advised to reduce CO₂ emission, such as improving manufacturing processes, concentrating more production in the most efficient plants, optimising the composition of the products, using improved products and valorising wastes in the production process.

Within the context of valorising wastes in the production process, the suggestion of CEMBUREAU is to use certain wastes as alternative fuels or raw materials, especially

considering that the industrial wastes are CO₂ neutral as conversion of limestone to CaO has already been performed during the thermal processing. Therefore, replacing the raw materials with secondary raw materials, such as battery recycling slags, and avoiding thermal processing, significantly reduces the CO₂ emission and non-renewable resources consumption.

Valorisation of lithium

Recently, interest in cradle-to-cradle Lithium recycling has substantially increased. Two reasons are generally given. First of all, the fast-growing increase in the need of portable batteries can put the long-term availability of primary Lithium at stake. Secondly, Lithium sources are unevenly distributed in the world with no active exploitation of Lithium sources in Europe. LIPEC, has been named as the successor of OPEC. Therefore, Umicore has developed a flowsheet to recover Lithium from the battery recycling slags.

Figure 5 presents a possible flowsheet consisting of eight unit operations. In a first step, the slag is milled to obtain a micro-meter sized powder. This powder is then leached in a sulphuric acid or hydrochloric acid medium at 80°C (step 2). Good Lithium yields are obtained with both media at free acid concentration of ~10 g/L. In order to ensure good filtration, the leach solution is neutralised in step 3 to obtain a solution at pH 4.5. Aluminum, the main impurity in solution, is removed under these conditions. Several neutralisation agents could be used. In a sulphate medium, CaO has the advantage that CaSO₄ is formed, which reduces the salt load of the solution. In a chloride medium, NaOH is preferred over CaO because Ca is more difficult to separate from Li. Na₂CO₃ can be used as neutralisation agent in both media but could decrease the Lithium yield of the process if it is already used in this stage of the flowsheet. After the removal of Aluminum by filtration, it is advantageous to increase the Lithium concentration in solution by using the filtrate again in the next leach operation a few times until the Lithium concentration is high enough for the next steps.

When the desired Lithium concentration is reached, the leach solution can be essentially purified of other metals in steps 5 and 6 by precipitation between pH = 8.5 and 9.5 with Na₂CO₃. This is an efficient way to remove Ca and Mg by forming their carbonate salts. Ca and Mg carbonate salts are less soluble than Li₂CO₃.

Finally, pure Li₂CO₃ is precipitated at high temperature (between 80 and 100°C) and pH. The solubility of Li₂CO₃ decreases at higher temperature (lower *K_{sp}*) and higher Na₂CO₃ content (common ion effect). Moreover the Lithium yield in this step (expressed as output of Lithium in Li₂CO₃ residue versus total output of Lithium)

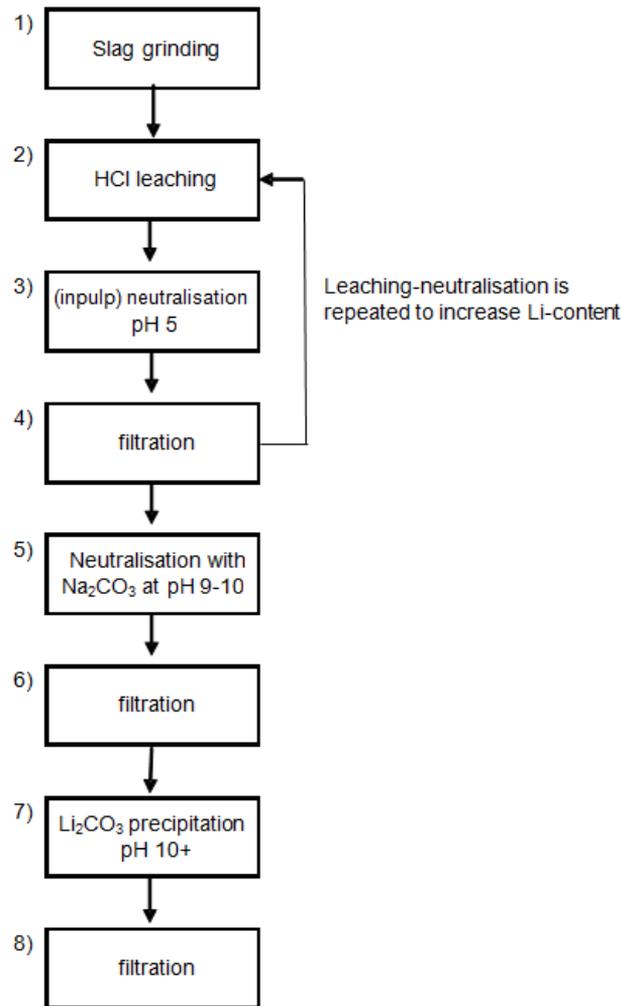


Figure 5: Flowsheet for the recuperation of Li_2CO_3 from Lithium containing slags

increases at higher initial Lithium concentration (filtrate of step 6). Therefore, the yield can be improved if water is removed from the solution between step 6 and 7 (e.g. by evaporation).

Conclusions

With its new battery recycling smelter in Hoboken, Umicore truly closes the materials loop from battery to battery for Li-ion and NiMH batteries. The newly developed flowsheet is virtually residue-free and valorises the majority of the valuable metals in end-of-life rechargeable batteries from a variety of appliances ranging from mobile phones over laptops to hybrid and electrical vehicles. In this paper the battery loop was discussed with special attention paid to the valorisation of the slag phase for construction applications and in terms of lithium recovery. With the expected

booming of e-mobility, the amounts of end-of-life batteries to recycle will rise drastically in the coming years. Umicore is ready to tackle the recycling process.

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