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INDUSTRIAL PROCESSING OF SPENT PORTABLE LITHIUM BATTERIES – A BRIEF OVERVIEW

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Abstract

The contribution deals with current state of spent portable lithium battery (SPLiBs) recycling in the industrial scale and provides a short overview of the existing industrial facilities. In general, SPLiBs processing consists of pre-treatment, including dismantling and mechanical treatment, pyrometallurgical processes and hydrometallurgical processes. In industry, these methods are most often combined. SPLiBs are usually processed together with other types of lithium batteries. The output of the processing is usually metal alloys based on Co-Ni-Cu for further processing, metal compounds such as Li_2CO_3, $Co(OH)_2$ serving as precursors for the production of new cathode material or directly new cathode material.

***Keywords**: spent portable lithium battery; recycling; pyrometallurgy; hydrometallurgy*

1. INTRODUCTION

Production of spent lithium batteries (LiBs), mainly rechargeable, is growing every year as a result of the boom in IT and telecommunication technologies and the expansion of electromobility supported by the European Union (EU). Currently, mainly portable and industrial LiBs are available on the waste market, but LiBs from electric vehicles (EVs) and hybrid electric vehicles (HEVs) are expected to start increasing rapidly in the near future. SPLiBs contain a mix of valuable metals some of which are part of the EU's list of critical raw materials in terms of supply risk and economic importance, highlighting the importance of spent LiBs recycling.

Nowadays, extensive research is being carried out worldwide for the recycling of all types of LiBs with the aim of complex processing and the extraction of the maximum amount of present metals and other materials, such as Co, Li, Ni, Al, Cu, separators and so on. In the industry, pyrometallurgical and combined processing of SPLiBs is still predominant. These are mostly "in-house" developed methods. The aim of this contribution is to summarize the available information and provide a brief overview of current technologies and trends in SPLiB recycling on practical scale.

2. COMPOSITION OF SPLiBs

Material composition of portable rechargeable LiBs is in Table 1. [1].

Table 1. *Material composition of portable rechargeable LiBs*

Components	Material	Content [%]
Cover	Steel, aluminium	20-25
Cathode active material	$LiCoO_2$, $LiNiMnCoO_2$, $LiFePO_4$, $LiMn_2O_4$,	25-35
Anode active material	Graphite	14-19
Cathode	Aluminium	5-7
Anode	Copper	5-9
Separator	PP, polyethylene (PE)	1-4
Electrolyte	$LiPF_6$ dissolved in PC, EC, dimethyl carbonate	10-15
Additives	Carbon black, silicone, etc.	unspecified

3. THE POSSIBILITY OF SPLiBs PROCESSING

A general scheme of the processing of SPLiBs in an industrial scale is shown in Figure 1.

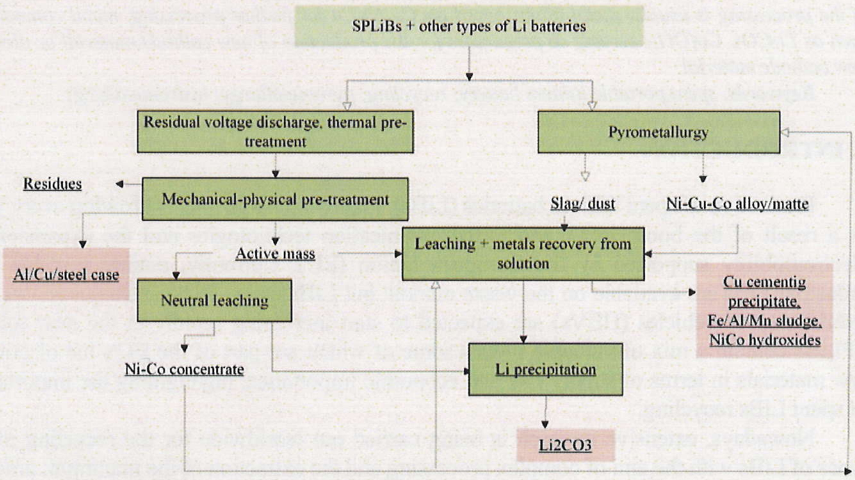

Figure 1. *General scheme for industrial SPLiBs recycling*

The mechanical-physical pre-treatment of SPLiBs is a key to efficiently obtaining the individual components and fractions that can be successfully recycled in own recycling process. Several mechanical pre-treatment processes have proven their suitability to obtain active mass containing Co, Li, Mn, Ni, etc., packaging materials, metal electrodes and other fractions with high efficiency and purity. Various combinations of crushing, grinding, sieving and other sorting steps (magnetic separation, vibrating sorting, different density sorting, etc.) are part of the proven processes. The advantage of mechanical processing is the concentration of metals into individual fractions. On the contrary, the disadvantage is the loss of materials in the process.

Nowadays, pyrometallurgical processing of spent LiBs is the most widely used in the industry. The resulting metal alloys or matte proceed to hydrometallurgical processing. The main advantages of pyrometallurgical processes are: high input variability, the relative simplicity of the process, high capacities, etc. However, there are more disadvantages, mainly high investment and operating costs, loss of metals and other materials in the process, emissions, risk of explosion and a necessity of refining obtained products.

Compared to pyrometallurgy, hydrometallurgical processes offer several advantages, for example lower investment and operating costs, higher yields and lower metal losses in the process, low production of gaseous emissions. The main disadvantage is the production of large amounts of waste water and solutions. However, they can be successfully recovered and reused in the process in many cases.

The input for hydrometallurgical processing is usually an active mass of SPLiBs, industrial LiBs or intermediates from pyrometallurgy. There are a number of different leaching systems that are suitable for leaching Co, Li, Mn and Ni from active mass, e.g. H_2SO_4 with added H_2O_2, HCl, H_3PO_4 with added H_2O_2, and others. In several media, quantitative conversions of metals to leachates can be achieved. However, the disadvantage is low selectivity.

For metals recovery from obtained leachate, combination of precipitation and solvent extraction (SX) in varying order has proven effective. By SX high efficiencies can be achieved. The problem is the requirement to repeat the individual operations in a multi-step process, which makes the extraction process longer and more expensive. The disadvantage of SX is also the cost of reagents and the necessity of their regeneration. However, regeneration can achieve cost savings and increase environmental acceptability as well.

4. INDUSTRIAL PLANTS FOR SPLiBs RECYCLING

Worldwide, there are several SPLiBs recycling companies and their number is growing. Several of them are operating as pilot plants (LithoRec, OnTo). In addition to SPLiBs, other types of lithium batteries are also an input – mainly LiBs from electromobility (in Accurec Recycling, Glencore, INMETCO, Recupyl Valibat, Retriev Technologies, etc.), or nickel batteries (in Umicore Baterry Recycling). Some plants deal only with mechanical-physical treatment (Batreg AG, Akkuser) and sell obtained fractions for further use. There are increasing facilities focusing on recycling waste from battery production (e.g. JX Nippon).

A brief review of existing industrial plants for spent LiBs recycling, their inputs and outputs, methods of processing and capacities, is listed in Table 2.

Table 2. *Summary of recycling plants for spent LiBs recycling [2-18]*

Company	Input	Processing	Output	Capacity [t/yr]
Accurec Recycling, Germany	All types od spent LiBs	Combined	Co-Ni-Mn-Fe alloy; Li_2CO_3	3000
AkkuSer, Finland	All types od spent batteries	Mechanical-physical pre-treatment	Metals fractions	4000
Batrec AG, Switzerland	All types od spent batteries	Mechanical-physical pre-treatment	Metals fractions	200
Glencore, Canada	Spent rechargeable LiBs	Combined	Co compounds Li slag	7000
INMETCO, USA	Spent rechargeable LiBs	Pyrometallurgy	Co-Ni-Fe alloy	6000
JX Nippon, Japan	Production waste	Pre-treatment Hydrometallurgy	Electrolytic Co, Ni $MnCO_3$, Li_2CO_3	5000
Recupyl Valibat, France	Spent rechargeable LiBs	Pre-treatment Hydrometallurgy	Electrolytic Co $Co(OH)_2$, Li_3PO_4	110
Retriev Technologies, Canada	Spent LiBs	Combined	$LiMeO_2$, Li_2CO_3, graphite	4500
SNAM, France	Spent rechargeable LiBs	Thermal pre-treatment Hydrometallurgy	Saleable products of Co and Li	300
SMM, Japan	Spent rechargeable LiBs	Combined	Cathode active material	n.d.
Umicore Baterry Recycling, Belgium	Spent rechargeable LiBs, Ni-Cd, NiMH batteries	Combined	$LiCoO_2$ $Ni(OH)_2$	7000
LithoRec, Germany	Spent rechargeable LiBs from EV	Pre-treatment Hydrometallurgy	Cathode active material	2000
OnTo, USA	Spent rechargeable LiBs from EV	Pre-treatment Hydrometallurgy	Cathode/anode material	n.d.

5. CONCLUSION

Material recycling of SPLiBs has been carried out around the world for several years. However, in the context of their increasing consumption, it is necessary to increase capacities, streamline processes, adapt technologies to other types of spent LiBs, e.g. LiBs from EVs. A comprehensive approach is preferred with the aim of maximising the recovery of present components. The main challenge in recycling processes is to achieve high selectivity and efficiency of individual processes. The demand for high selectivity results from the heterogenity of the composition of the spent portable LiBs, which represent a wide mixture of materials. EU legislation defines a minimum recycling efficiency of 50 % for spent Li cells and up to 65 % in 2025. In the case of pyrometallurgy, where the graphite and separator is combusted and some metals e.g. Li and Al are lost in the slag, achieving the required recycling efficiency is questionable. From this point of view, hydrometallurgical treatment processes can be considered more appropriate. Hydrometallurgy achieves high metal yields at low losses, the processes are more flexible, more environmentally friendly and energy efficient. However, they have usually a lower processing capacity compared to pyrometallurgical processes However, the lower processing capacity can partly be considered as an advantage due to the high process flexibility.

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