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Economic and Environmental Sustainability of an Innovative Cryo-Mechano-Hydrometallurgical Process Validated at Pilot Scale for the Recycling of Li Batteries

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Abstract: An innovative cryo-mechano-hydrometallurgical process (named LIBAT) was demonstrated at pilot scale for the treatment of EOL lithium primary batteries with chemistry Li(0)-MnO₂. The process allowed the recycling of steel scraps from external cases after cryomechanical dismantling, and the recovery of Mn and Li products after hydrometallurgical processing. During demonstration activities, about nine tons of batteries were treated in the cryomechanical section, and one ton of black mass was treated in the hydrometallurgical section for the recovery of Mn hydroxides and Li₂CO₃. The environmental impacts of the process were evaluated in comparison with an innovative pyrometallurgical approach allowing Li recovery, confirming the benefits of the proposed process due to a reduction in energy consumption. Process simulations were performed considering different mixture feeds (only Li primary, or mixture with Li-ion batteries) and process options (only the cryomechanical section of the integral process) to assess the lower limits of potentiality that would ensure economic sustainability.

Keywords: Li primary batteries; recycling; hydrometallurgy; life cycle analysis; process analysis



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1. Introduction

End-of-life (EOL) primary batteries of Li(0)-MnO₂ are an environmental problem due to their low value content and to the dangerous materials they contain (Li(0) and the flammable solvents of the electrolytes) [1].

These aspects have depressed research on Li(0) recycling, with all the attention being dedicated to Li-ion batteries, which also contain the same flammable solvents but are more widely diffused on the market and contain valuable metals such as Co, Ni and Cu [2].

Li(0) batteries are currently a cost for battery collectors, who after manual sorting of the different battery types, can obtain revenues from some types (Li-ion batteries), but must pay smelters for the disposal of others (Li(0) type).

The research gap addressed in this paper is the lack of a process able to treat the Li(0)-MnO₂ battery type and ensuring effective material recovery.

In fact, the most commonly adopted treatment for EOL batteries in the EU is the pyro-metallurgical one in which whole batteries, or some battery fractions, are smelted at high temperature (1500 °C) with other solids [3]. This leads to the downcycling of the main battery components of Li-MnO₂ batteries, such as lithium, manganese and iron, which are lost in the slag [4].

Only a few works can be found in the literature addressing Li(0) treatment, with Li-ion being the most diffuse and targeted technology both in manufacturing and recycling. These few works use thermal processes for battery deactivation [5–9], or for direct dismantling [10,11], followed by hydrometallurgical operations.

All these works have operated at lab scale without evaluation of heterogeneity effects and impurity effects on final product composition [5,6,8–11], or in pilot scale [7], but without reporting analyses of environmental and economic impacts.

A patent survey was also performed evidencing that Toxco company developed a combined hydro-pyro-metallurgical process for Li recycling from Li(0)-containing wastes including primary batteries [12]. Nevertheless, to the best of the authors' knowledge, no process or plant is now operating in the EU for dedicated hydrometallurgical treatment of Li(0) primary batteries, and no economic analysis or LCA is available regarding these batteries except a previous preliminary process analysis reported from one group [13].

In this context, this work presents an innovative process for treating Li(0) batteries and recovering all their valuable components. In particular, the demonstration of the process at pilot scale is reported, evidencing its technical feasibility in terms of the safety of the cryomechanical opening of batteries, and also for the assessment of metal impurities in the final products.

The proposed process is able to recycle the different components of Li(0) batteries (steel scraps, Mn and Li products) in a sequence of physical and chemical operations. The technical solution for the treatment of Li(0) batteries includes a cryomechanical treatment that avoids fire and explosions due to residual Li(0) (present in EOL primary batteries because of incomplete discharge) and the flammable solvents used to dissolve electrolytes in all Li batteries. In this way, the safe liberation of battery components is achieved and, after dry separation, fractions are neutralized in water for safe Li(0) oxidation and dissolution. Electrode materials rich in Li and Mn can then be fed to the hydrometallurgical section, where products of Mn and Li can be recovered for the manufacturing of new electrode materials. The specific combination of cryomechanical and hydrometallurgical operations here reported can be used also for the treatment of other types of batteries, such as Li-ion batteries, which present similar chemical composition and safety issues. Li-ion batteries contain also other valuable materials (copper, aluminum, cobalt, nickel, graphite) which can be recovered according to the same sequence of operations used for Li(0)-MnO₂ batteries [14,15].

Specific contributions of this work include an environmental analysis performed by LCA, comparing this process with landfilling and pyrometallurgical treatment, and economic analyses performed on the basis of experimental results elaborated as mass and energy balances and considering different process conditions in terms of sequence of operations (only cryomechanical, or the complete process), feed (only Li(0), or mixed Li(0)-Li-ion), and potentiality.

This work is a continuation of two previous works addressing upcycling of LiMnO₂ for the resynthesis of LiMnPO₄ electrode nanomaterials [16], and reporting a preliminary process simulation of the same process before demonstration campaigns were concluded [13]. In particular, in [13], preliminary data from the cryomechanical section were used along with lab-scale data for the hydrometallurgical section because the pilot-scale prototype was not yet started up. Preliminary process analysis was performed considering only Li(0) feed with different potentialities (up to 900 ton/y) showing how economic feasibility changes with these conditions [13].

In the present paper, final mass and energy balances from demonstration campaigns were adopted, economic analysis was performed for a mixed feed of Li(0) and Li-ion batteries, and environmental impact assessment by LCA was reported for the first time both for the LIBAT process and for an innovative pyrometallurgical process aiming at Li recovery.

2. Materials and Methods

2.1. Materials

EOL Li(0) batteries were manually sorted by S.E.Val. staff and then further classified in order to separate Li(0)-MnO₂ chemistry from thionyl chloride and iron disulfide types, which were not specifically addressed in this study. Li(0)-MnO₂ types were further sorted as

coin type and button type by sieving. Demonstration activities were then performed using 1:1 mixtures of coin and button cells of Li(0)-MnO₂ type. During all the demonstration activities, a total amount of 8900 kg of Li was used.

2.2. Process Demonstration and Product Characterization

The proposed process included two main sections specifically designed and constructed by Eco Recycling staff: a cryomechanical section and a hydrometallurgical section, as detailed in the block diagram in Figure 1, in which also the material flow and energy consumption are reported, based on a feed of 100 kg batteries per batch.

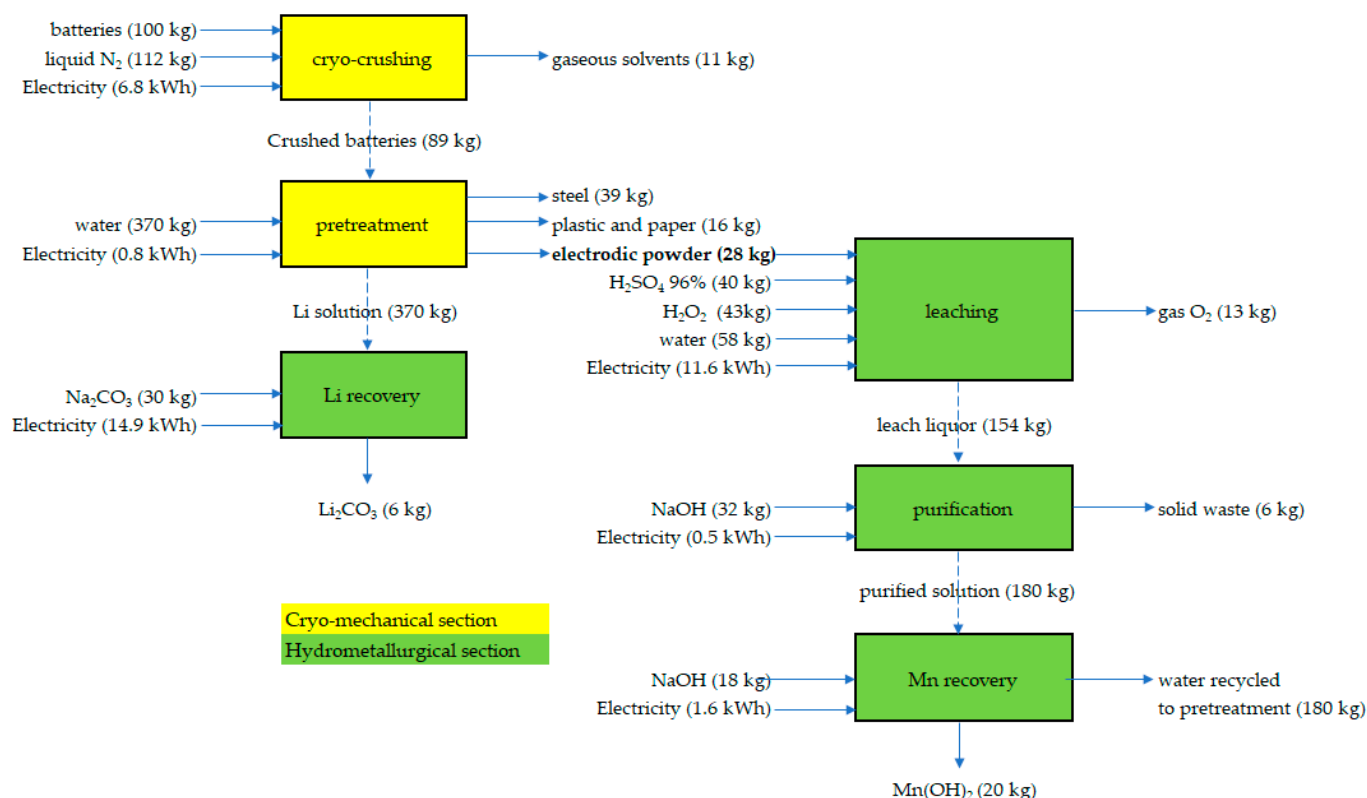


Figure 1. Process flow diagram for the cryomechanical and hydrometallurgical sections of the process for Li(0) recycling.

The cryomechanical section (400 kg/day potentiality) included a cryogenic pre-treatment performed on the batteries in order to prevent explosions and control flame formation during crushing. Thermally stabilized batteries (−80 °C for 45 min using a N₂ liquid shower in a cabinet) were then crushed in a hammer mill with 10 mm under-sieve. Crushed material was sieved (1 mm) and the oversieve was separated by magnetic separation using a magnetic overbelt placed above the sieving belt. After this treatment, three fractions were collected: a fine powder made up of electrode materials, a coarse magnetic fraction made up of external steel cases, and a non-magnetic coarse fraction made up of separators of plastic and papers. All these fractions were periodically sampled and characterized for their chemical composition by digestion and analytical determination of metal in solution by atomic absorption spectrophotometer (ContrAA 300—Analytik Jena AG, Jena, Germany).

All fractions were then neutralized in water to dissolve residual Li(0), giving three Li-bearing streams joined together and used for Li recovery in the hydrometallurgical section.

The hydrometallurgical section included:

- Lithium recovery from neutralization waters by precipitation as Li₂CO₃.

- Manganese extraction from neutralized electrode powder.
- Manganese-bearing solution purification.
- Manganese recovery by precipitation as manganese hydroxides.

The lithium-bearing solutions obtained after neutralization constituted the feedstock for the lithium carbonate precipitation reactor. Here, after sodium carbonate addition, lithium carbonate precipitated due to its low solubility when the mother solution was heated. After precipitation, the final Li product was recovered by filtration.

The neutralized electrode powder was fed to the leaching reactor for Mn extraction using H_2SO_4 and H_2O_2 . Extraction of Mn was linked with solubilization of Fe coming from external case steel impurity ending in the electrode powder. Fe was removed by selective precipitation tuning leachate pH. Iron hydroxide and the insoluble residual carbon fraction were separated by filtration of the leachate. Manganese hydroxide was precipitated by increasing the pH of the Mn-bearing solution. After precipitation, the final Mn product was recovered by filtration.

Li and Mn products were characterized by X-ray diffraction (Rigaku, D-Max Ultima – Rigaku Corporation, Tokyo, Japan) and chemical composition by digestion and atomic absorption spectrophotometry.

2.3. Life Cycle Assessment

On the basis of mass and energy balances obtained during demonstration activities, the environmental impact of the developed process was assessed by life cycle impact assessment (LCIA), which includes both classification and characterization steps and normalization and weighting phases. The study was carried out using the Gabi Software System and Database for Life Cycle Engineering (version 10.6.2.9, Sphera Solutions GmbH, Leinfelden-Echterdingen, Germany) integrated with Professional Database v. 2022.2, used for the production processes of energy and raw materials and the quantification of the environmental impact of treatments, following the recommendation of the ISO 14040:2006 norm. The impact categories and the related characterization methods were selected in agreement with the Product Environmental Footprint (PEF) guidelines (environmental categories, recommended models at midpoint, together with their indicators, characterization factors, units and sources) and in accordance with the nomenclature and properties of the International Reference Life Cycle Data System ILCD recommendation. In this regard, the ILCD Handbook represents the basis of the EF method. The analysis considered the impacts on the categories of acidification terrestrial and freshwater, climate change, ecotoxicity freshwater, eutrophication (freshwater, marine, terrestrial), ionizing radiation (human health), land use, cancer/non cancer human health effects, ozone depletion, photochemical ozone formation (human health), resource use, energy carriers, resource use minerals and metals, respiratory inorganics and water scarcity. The normalization and weighting step allow the determination of the relevance of the different environmental impact categories. Although they are not mandatory, normalization (“calculating the magnitude of category indicator results relative to reference information”) and weighting (“converting and possibly aggregating indicator results across impact categories using numerical factors based on value-choices”) are strongly recommended. They allow a global assessment to both overcome the possible heterogeneity of classification and characterization results and compare the criticality of the different environmental aspects.

Environmental impacts of the proposed process were compared with the other two scenarios, which considered landfilling and an innovative pyrometallurgical approach developed by Accurec at pilot scale [8]. In this innovative pyro-metallurgical process, exhausted batteries are fed to a vacuum pyrolysis heat treatment for their deactivation, an alternative to the N_2 shower in the LIBAT process. The gaseous compounds produced in this step are re-condensed to produce crake oil. The deactivated batteries are fed into two consecutive grinding steps and then to size separation for the recovery of the steel coarse fraction from the fine electrode powder. This powder is then pelletized with bentonite binder and fed to an oven in a nitrogen atmosphere in which the lithium is reduced,

evaporated (1342 °C) and then recovered by condensation [8]. In the impact evaluation, the solids leaving the furnace are fed to the hydrometallurgical treatment according to the same process as in the LIBAT process. In Table A1, mass and energy balances for the pyro-metallurgical process used in this evaluation are reported as elaborated according to information extracted from the literature [8] and thermodynamic simulations. For the LCA of the LIBAT process, also thermal valorization for the non-magnetic coarse fraction made of plastic and paper was considered.

2.4. Process Simulations

The process was simulated in batch mode using SuperPro Designer 12 (Intelligen, Inc., Koch Plains, NJ, USA). The multi-parametric analysis was performed by simulating the complete process (cryomechanical followed by hydrometallurgical process for Mn and Li recovery), or a part of it (cryomechanical section and Li recovery), and varying the following inputs:

- Different plant potentialities in the range of 12–550 t/yr.
- With and without the “consortium fee”, the fee paid by consortia and local authorities to private recycling companies performing the end-of-life treatment of batteries.
- Different “treatment fees” paid for end-of-life battery treatment by private customers, i.e., battery collectors not having dedicated infrastructures for the treatment of Li(0) batteries.
- Different feed compositions (only Li(0), and mixtures of Li(0) and Li-ion with a 1:10 weight ratio).

Mass and energy balances were obtained for cryomechanical treatment and hydrometallurgical treatment after the demonstration at pilot scale, as reported in Figure 1.

Capital investment was estimated for the different potentialities, using a power scaling law with 0.6 exponent starting from EUR 320,000, which was the cost of the pilot plant built.

Operating costs of chemicals, waste and wastewater treatment, and electric energy were set on the basis of costs sustained during the demonstration, while prices of the products were estimated on the basis of market analysis (as reported in Table A2).

The economic feasibility of the process was assessed using various measures of economic profitability such as gross margin and payback time (PBT).

The gross margin is a measure of profit that tells what portion of the revenues becomes gross profit. It is calculated as the ratio between gross profit and revenues, as in (1):

$$\text{Gross Margin (\%)} = (\text{Gross profit}) / \text{Revenues} \times 100 \quad (1)$$

which, for the definition of gross profit as revenues minus annual operating costs (AOC), becomes:

$$\text{Gross Margin (\%)} = (\text{Revenues} - \text{AOC}) / \text{Revenues} \times 100 \quad (2)$$

The PBT refers to the amount of time needed to recover the cost of the investment.

$$\text{PBT} = (\text{Average annual cash flow}) / (\text{Cost of investment}) \quad (3)$$

The cash-flow analysis was conducted under the assumption of an inflation rate of 1%, an income tax of 40% and a depreciation time of 7 years. Such a depreciation time was set based on an overall plant depreciation coefficient of 15%. Such a coefficient value was adopted based on current Italian legislation (Ministerial Decree 31 December 1988) that sets as 10% the depreciation coefficient for large mechanical machines, 12% for electricity generation plants, engines and pumps, and 17.5% for chemical equipment within the metallurgy industry.

More detailed information on process economics can be found in the relevant literature [17].

3. Results

3.1. Process Demonstration and Product Characterization

The analysis of the batteries manually sorted at S.E.Val. as Li(0)-MnO₂ type denoted the presence of two main formats: coin cells (33% as weight) and cylindrical cells (67%). These formats have different sizes and were easily separated by sieving, and dedicated tests using single type feed denoted different contents of Li ranging from 0.7 to 2.4% in coin and cylindrical type, respectively. Due to the simplicity of format separation by sieving, and for security reasons, the shredding activity recombining battery formats in a 1:1 ratio was performed in order to have standard composition and then controlled conditions during cryo-milling and Li-neutralization.

In these conditions, the batches of batteries were fed to the cryomechanical section and separated by sieving and magnetic belt, giving the three fractions with % weight distribution and composition reported in Table 1.

Table 1. Weight distribution and chemical composition of the three fractions obtained after cryomechanical treatment and dry separation.

Fractions	[%]	Li [mg/g]	Mn [mg/g]
Electrode Powder	32 ± 9	40 ± 2	364 ± 6
Magnetic Fraction	39 ± 7	6 ± 7	6 ± 1
Non-Magnetic Fraction	16 ± 2	29 ± 7	288 ± 76

Chemical characterization of samples from these fractions evidenced a high content of Li and Mn in the electrode powder, as expected, but also in the non-magnetic coarse fraction, due to residues of electrode powder still adhering to plastic and paper layers. About 64% of the weight of the non-magnetic fraction was made of this residual electrode powder, which was then separated and recovered after neutralization in the bottom of the reactor.

During the demonstration activities, a total of 8900 kg of batteries were treated, producing the following solid fractions: 3450 kg of steel scraps, 2800 kg of electrode powder and 1400 kg of non-metal fraction; this last fraction included still adhering electrode powder, which was separated from the plastic and paper in a neutralization bath.

The distribution of processed batteries among mechanical section outlet streams was then: 32% fine fraction (electrode powder), 39% steel and 16% non-metals. A total of 64% of this last fraction was indeed electrode powder recovered after neutralization, so another +10% should be considered for the fine fraction, which then would have reached 42%. Therefore, the % distribution of the different fractions emerging from mechanical treatment was 42% fine fraction, 39% iron and 6% non-metals. A weight loss of 14% was registered mainly related to organic solvents evaporated and entrapped by the gas treatment unit operating in the industrial site.

As for the hydrometallurgical section, Li₂CO₃ was recovered from washing waters, obtaining 2.7 kg of Li₂CO₃ per 100 kg of Li(0)-MnO₂ treated batteries (56% of the total Li in batteries) with a precipitation yield of 70%. Li₂CO₃ purity could be increased from 97% to 99.8% by removing sodium impurities in filter press washings at the expense of the Li recycling rate, which was 39%.

The electrode powder was also fed to the hydrometallurgical section for Mn hydroxides recovery. Under optimized conditions, the recovery of 20 kg of Mn hydroxides per 100 kg of Li(0)-MnO₂-treated batteries was achieved, corresponding to a recycling rate of 94% for manganese.

As with the solid composition, Mn hydroxide purity could be increased up to 98.7% by washing in filter press, but without a recycling rate decrease.

During the demonstration, lithium was recovered by neutralization baths; as reported above, Li dissolved in this phase was about 56% of the total Li in batteries, thus limiting

the Li recycling rate. In order to increase the Li recycling rate, it was also recovered after Mn recovery from the Li-bearing effluents, using these effluents instead of water in the neutralization reactors. Consequently, a further increase in the Li recycling rate was obtained (+29%), reaching a 68% recycling rate and without changes in the final purity of the carbonate. Reusing Li-bearing effluents in the neutralization section also allowed a reduction in water consumption.

Mn and Li products were also characterized by X-ray diffraction, evidencing relevant peaks of Mn_3O_4 and Li_2CO_3 phase, respectively (Figure 2); then, in the case of Mn hydroxides (generally amorphous products), the presence of both Mn(II) and Mn(III) could be assumed due to partial oxidation of Mn during precipitation.

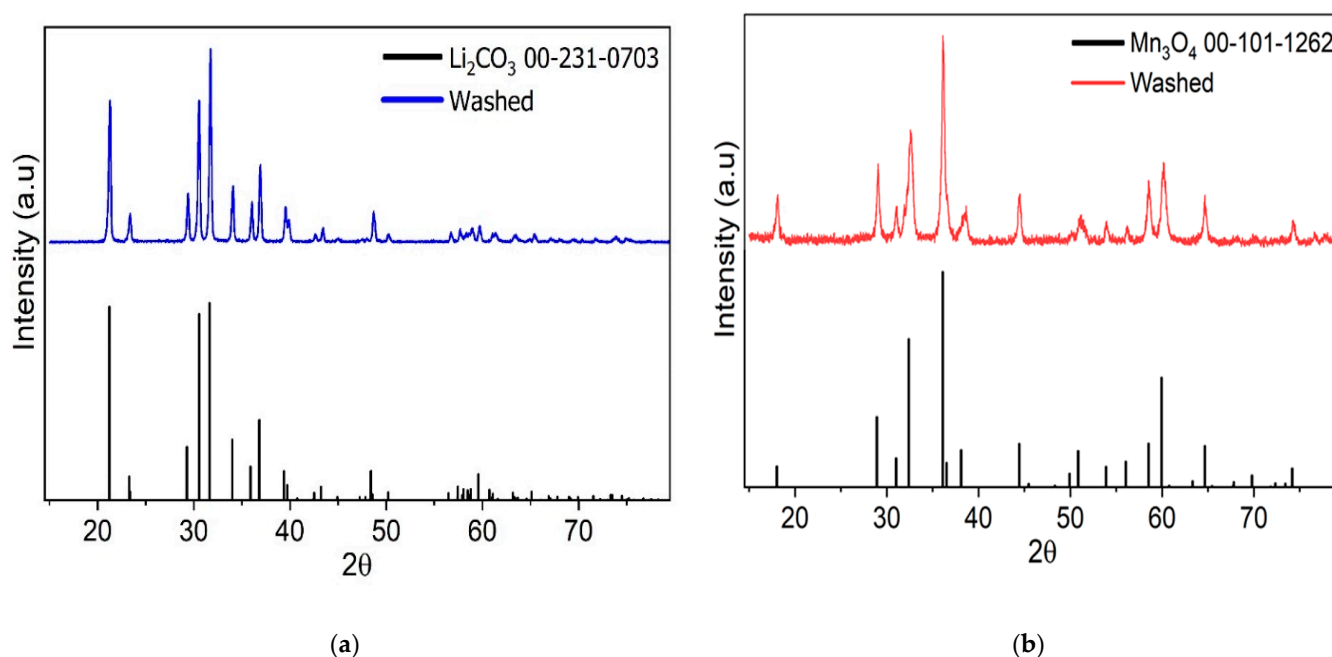


Figure 2. X-ray diffraction spectra of washed products: Li_2CO_3 (a) and Mn hydroxides (b) after washing in filter press.

The mass balances denoted that the overall recycling rate of the process (given by the recycling of steel scraps, Mn and Li products) was 65%.

3.2. Life Cycle Assessment

In order to compare the environmental impacts of the proposed process with possible alternatives, a dedicated analysis was performed using LCA for two other scenarios: landfilling and a pyrometallurgical approach.

This comparison was necessary because, in the literature, no available environmental analysis has been found for a Li(0) recycling process, as attention to Li-containing batteries is mainly focused on Li-ion batteries. The LCA results for Li-ion batteries cannot be compared with Li(0) batteries because these types of batteries present different chemical composition. Literature analysis evidenced the effect of chemical composition even inside the class of Li-ion batteries due to the heterogeneity of chemistry of cathodic materials which affected the impact categories in different ways [18,19].

Therefore, in order to have a suitable comparison with the proposed process, LCA was performed also for an advanced pyrometallurgical process developed by Accurec at pilot scale [8]. This choice was motivated by the fact that conventional pyrometallurgical processes currently used for Li-ion batteries are not suitable for treating Li(0)- MnO_2 primary batteries. In fact, Li(0)- MnO_2 primary batteries consist of Fe, Li and Mn, and feeding the whole batteries into the furnace (as in the case of Li-ion batteries) would mean losing Fe, Li

and Mn in the slag, and then all the components are lost in slag without any recycling. In fact, re-dissolving such slag for metal recovery is not convenient and the metal-containing slag is generally used as concrete additive for building materials or road pavements (downcycling). The alternative pyrometallurgical process used as a comparison for the LIBAT process includes high temperature deactivation of the batteries for dismantling and component liberation, and then high temperature pyrometallurgical treatment for Li reduction, volatilization and condensation. In this way, Li can be recovered and the residue treated according to the same hydrometallurgical treatment proposed in LIBAT. Therefore, the advanced pyro- process here considered as a comparison allows the recycling of the same metals as the LIBAT process.

The LIBAT process impact showed negative values (credits towards the environment) in many categories: acidification, cancer human health effect, eutrophication (both marine and terrestrial), land use, ozone depletion, photochemical ozone formation, resource use and respiratory inorganics. This result was mainly due to the recycling of lithium, manganese and steel scraps. The avoided impacts resulting from material recycling overcome the emissions of the process. Furthermore, there was also a positive effect for the environment due to the plastic exploitation for energetic scopes.

Considering the loads of the LIBAT process, the chemicals used in leaching had the highest environmental loads in most categories. This was due to the use of hydrogen peroxide, which accounted for an 80% contribution to the load of the leaching process. In fact, even if H_2O_2 does not produce any toxic residue in redox processes, its production is energy intensive and requires the use of catalysts, which are critical raw materials. Its use in the process thus heavily weighs down the load on the environment. One possible alternative reducing agent could be carbohydrates or organic acids, for instance from agro-industrial wastes, as green and sustainable reducing agents allowing Mn dissolution [20]. In addition, sodium hydroxide causes a relevant impact (with an average contribution in the whole process around 40%) in the categories of climate change, eutrophication, ionizing radiation, land use and photochemical ozone formation. Also in this case, an alternative precipitating agent could be used such as carbonate or oxalate to recover Mn from solution. As concerns the environmental assessment of the pyro- process, the main issue was related to energy consumption in the step of lithium recovery, and energy consumption affected almost all the impact categories. The energy consumption due to initial thermal deactivation and battery smelting (estimated by thermodynamic data) was dramatically higher with respect to cryo-crushing. LIBAT energy consumption was 13% of that used in the advanced pyro- process. Of course, this difference generated a cascade of negative loads for the pyro-process in the different impact categories.

As reported above, LCA allowed the estimation of process impacts in different impact categories; considering the traditional category of climate change, the LIBAT process allowed a 91% reduction of CO_2 emissions with 7.2×10^2 kg CO_{2eq} /ton batteries versus 8.4×10^3 kg CO_{2eq} /ton batteries in the advanced pyro-process.

The normalization and weighting steps offered an overview of the environmental load of the innovative treatment (Figure 3). The assessment produced a negative value, around -2.5 , which confirmed the environmental benefits of the process, thanks to the recovered fractions. A relevant environmental gain is highlighted in the category of cancer human health effects, mainly connected to the possibility of steel recovery. The most affected category identified was that of ionizing radiation, with leading contributions by both purification and leaching, which had 48% (mainly due to NaOH use) and 24% (due to both H_2O_2 and electricity consumption), respectively, of the total emissions in this category.

In order to have a comparison for all impact categories, an environmental performance index was evaluated for landfilling, the LIBAT process and the pyro-metallurgical process, normalizing and weighting the different impact categories. This index showed that landfilling had a load of 0.7, the pyro-metallurgical process had 2.9 (mainly due to energy consumption) and LIFE-LIBAT resulted in a credit of -2.5 towards the environment (Figure 4), confirming the benefits of the proposed process and the fact that using

a pyro-metallurgical approach has high impact due to high energy consumption which cannot be balanced by the environmental credit of recovered fractions. Furthermore, a sensitivity analysis was performed to estimate the necessary energy decrease needed to make the pyrometallurgical approach sustainable from an environmental point of view. The assessment (considering possible energy savings between 10 and 50%) showed that the balance between impacts and recovery benefit could be reached only by an energy reduction of 50%, which resulted in an index of -0.5 . This hypothesis, almost impossible to achieve at a real scale, confirmed the relevant advantage of the LIBAT option.

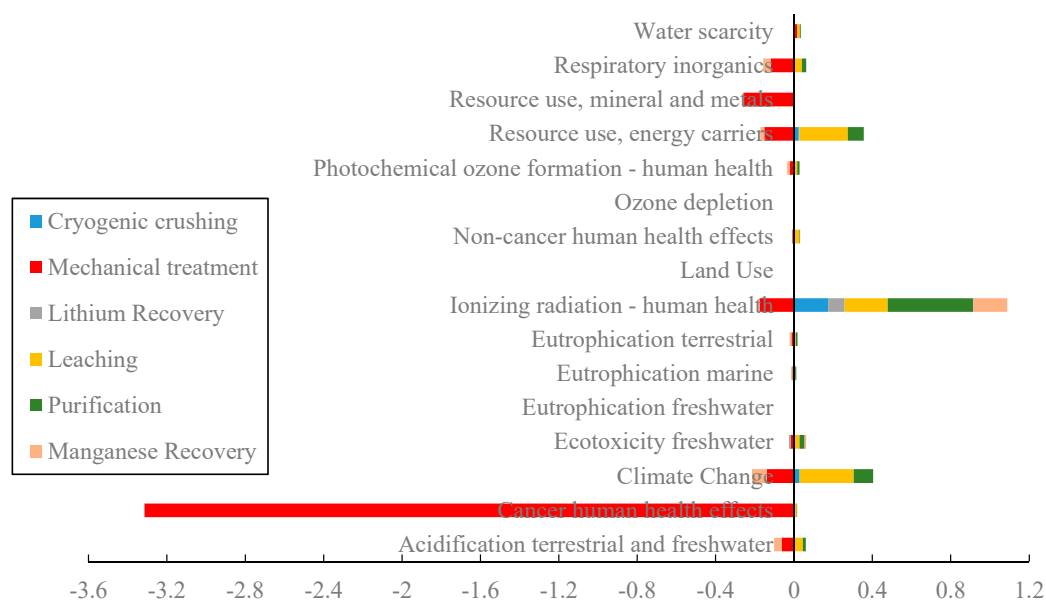


Figure 3. Results of normalization and weighting steps of LCA related to LiBat process (functional unit: 100 kg of treated waste).

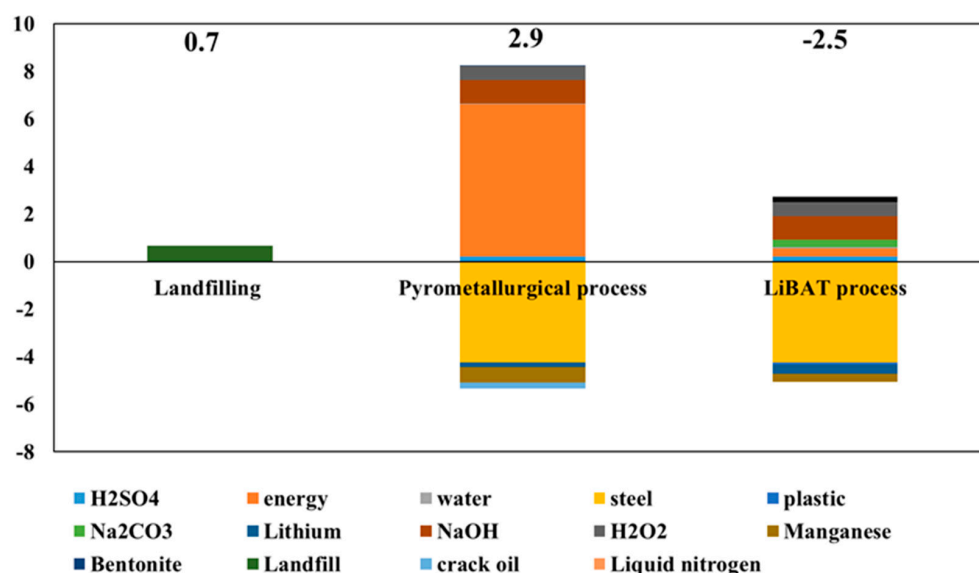


Figure 4. Environmental performance index comparison between landfilling, the LIFE-LIBAT process and the advanced pyro-metallurgical process, including Li reduction, evaporation and condensation.

These results were supported by the very good inventory data quality, confirmed by all the impact categories considered; by their temporal representativeness (data not older than 4 years); and by their technological and geographical representativeness (en-

ergy and mass balances were based on real experiments performed at pilot scale and on European territory).

3.3. Process Simulations

In process simulations, the current EU situation in EOL battery management was considered. Dedicated consortia and local authorities collect EOL battery mixtures and then pay EOL treatment performers; this is what is called a “consortium fee” and it is estimated around 0.4 EUR/kg according to the current quotation offered by S.E.Val. The following simulations were performed considering the consortium fee, but also the lack of this incentive that is a negative cost for battery recyclers.

The stocks of batteries taken by recyclers contain all types of batteries and require, as a first operation, a sorting according to the different chemistries, each one requiring a different EOL treatment. After this sorting, not all recyclers can treat all types of sorted batteries. Some kinds of batteries can be sold by a recycling company to others that are able to treat them. Li(0) batteries are one of the most difficult types to treat due to Li(0) and explosive solvents, but also due to their low intrinsic value compared with Li-ion batteries containing Co and Ni. Therefore, after sorting, battery recyclers typically pay specialized recyclers for treating Li(0) batteries; this is the “treatment fee” which, according to S.E.Val information, is currently 1.850 EUR/kg. In the following simulations, different treatment fees were considered in a competitive range according to the current price.

The products obtained by the developed process are steel scraps, Li_2CO_3 and Mn hydroxides. As for steel scraps, the recycling of ferrous metals is already a consolidated route with a market price of about 180 EUR/ton for these scraps [21].

As for lithium carbonate, the main application is in the manufacturing of Li-ion batteries, while minor applications are found in glass, ceramics and grease. As for its use in Li-ion batteries manufacturing, the production of materials is concentrated in few large enterprises (BASF, Umicore, Johnson Matthey). The Li carbonate obtained by the LIBAT process was suitable in terms of purity (>99%) and a commercial price of 59 EUR/kg was assumed [22].

As for manganese, it is mainly used in steel production starting from ores, while high purity Mn products (oxides and sulfates) are used in battery manufacturing (mainly alkaline and NMC Li-ion batteries, respectively) and fertilizers. As for NMC battery manufacturing (the Li-ion type used in electric vehicles and industrial batteries for energy storage from renewables), high purity Mn hydroxides obtained by the LIBAT process can be used as raw material for the production of high purity sulfate; the market price for Mn hydroxide can be estimated as 80% of that of the high-purity MnSO_4 used for LIB production (0.85 EUR/kg) [22].

Process simulations were first performed using the complete LIBAT scheme with potentialities ranging from 12 ton/y to 500 ton/y, and with negative costs for batteries ranging from 400 EUR/ton (the cost paid by consortia to battery recyclers for taking a battery mix) to 1500 EUR/ton (applying a competitive fee with respect to the current price asked by smelters for EOL Li(0) treatment, which is 1850 EUR/ton); these analyses showed that the process is economically sustainable for this range of potentialities, taking into consideration a cost of treatment (which will be a revenue for the battery recycler) lower than that currently paid for Li(0) treatment in pyrometallurgical processes. Nevertheless, the gross margin remains low, evidencing the low remunerability of the process.

Larger potentialities were not tested at this stage, even though the total amount of Li(0) in the EU can reach about 2000 ton/y, because it is not realistic that a new player can capture the whole market.

Other simulations were performed considering only cryomechanical treatment, neutralization and Li recovery, thus excluding Mn extraction and recovery and assuming disposal costs for the electrodic powder. In this case, the operating costs of the LIBAT process at prototype scale are competitive (lower) than those required by smelters for Li(0) treatment. Process simulations performed for different potentialities of the prototype (50

and 100 ton/y, corresponding to 200 and 400 kg/d) showed that operating costs diminished by revenues were lower than smelter prices (410 and 820 EUR/ton, respectively, versus 1850 EUR/ton for pyro- treatment). However, for these potentialities, with a negative cost for treatment of 400 EUR/ton, the process is not profitable yet. Nevertheless, by increasing the potentialities (to 300 and 500 ton/y) and considering a price for Li(0) treatment being paid to recyclers, the process becomes economically feasible for 300 ton/y and a treatment fee of 1500 EUR/ton (still lower than the smelter price) and the payback time is 2.85 years, while for 500 ton/y and a treatment fee of 1000 EUR/ton, the PBT is 4.03. These figures demonstrate the competitiveness of the LIBAT process against pyro-metallurgical treatment. Even in this case, gross margin values are comparable with the complete LIBAT process at the same potentialities.

Another set of simulations was performed considering the possibility of treating other types of wastes (Li-ion batteries) with the same process. In this case, simulations were performed considering typical weight ratios observed in the collected battery mix (Li(0):Li-ion = 1:10), mass balances from laboratory tests using Li-ion batteries cryo-crushed in the LIBAT prototype [23], and additional revenues from the Cu scraps (2.6 EUR/kg) [21], Al scraps (0.7 EUR/kg) [21], and graphite (7 EUR/kg) [22] present in Li-ion batteries. The final product of the hydrometallurgical section in this case was a mixed hydroxide containing nickel, manganese and cobalt (22.8 EUR/kg estimated market price, calculated as 80% of the commercial mixed oxide price, 28.5 EUR/kg [22]), which is the precursor for the production of cathodic material in NMC Li-ion batteries. In this case, considering only the negative cost received by recyclers for battery mix treatment (400 EUR/ton), the complete process was economically feasible with a payback time of 2.78 years for the 550 ton/y potentiality. This potentiality could be easily reached considering that about 3000 ton/y of Li-ion batteries are currently collected only in Italy. In this case, a significantly larger gross margin was estimated, evidencing the advantages in recovering high value products such as Li-ion battery precursors.

In Table 2, the main economic figures for the different simulations are reported.

Table 2. List of adopted conditions for process simulations performed.

Process	Feed	Potentiality (t/y)	Consortium Fee (EUR/kg)	Treatment Fee (EUR/kg)	CAPEX (kEUR)	OPEX (kEUR)	Gross Margin (%)	PBT (y)
LIBAT	Li(0)	12	0.4	0	320	58	−60.90	N/A
LIBAT	Li(0)	300	0	1	619	572	20.40	3.72
LIBAT	Li(0)	500	0	1	840	859	24.51	2.53
Cryo-mech	Li(0)	50	0.4	0	200	83	−33.23	N/A
Cryo-mech	Li(0)	100	0.4	0	200	125	−14.01	N/A
Cryo-mech	Li(0)	300	0	1	387	395	9.26	8.65
Cryo-mech	Li(0)	300	0	1.5	387	395	23.62	2.85
Cryo-mech	Li(0)	500	0	1	525	565	16.22	4.03
Cryo-mech	Li(0)	500	0	1.5	525	756	29.47	1.87
LIBAT	Li-ion + Li(0)	550	0.4	0	2.792	1.400	42.03	2.78

It should be noted that in these simulations, the potentiality was fixed on the basis of available information and estimates regarding the waste flux of Li(0) batteries in the EU. This amount is quite limited, thus also limiting the possible advantages in scale law for decreasing products' costs. Possible future improvements in waste collection schemes could lead to an increase in waste flows, and then also the construction of large-scale plants with a reduction in production costs. On the other hand, the outputs of the economic analysis were based on a preliminary optimization at pilot scale with equipment not fully automated or optimized as generally is the case in large scale. This would lead to a decrease

in operating costs for manpower, but perhaps also an increase in plant costs related to automatization and control. Finally, the economic figures were strongly affected by the revenues due to selling products and the battery market during the last year, which saw a significant increase in battery materials' costs; as an example, Li_2CO_3 increased from about 13 up to 67 EUR/kg during 2022. If these trends continue, considering the global investments in electric vehicles, the remunerability of Li-battery recycling processes will increase, allowing even small-scale plants to be distributed in the different countries, and thus not requiring high initial investment and simultaneously reducing the transport of hazardous wastes.

4. Discussion

The analysis reported in this work is a milestone in the development of hydrometallurgical processes for the treatment of Li(0) batteries. However, the process development for such complex wastes requires technical, economic and environmental validation in order to have a chance of being adopted in the future.

The implemented procedure for battery sorting and the optimization of the operating conditions in pilot scale evidenced that cryo-stabilization allowed safe operations for Li(0) batteries dismantling. This was the first step in the battery recycling process, allowing products to be obtained at pilot scale and thus assessing the effect of waste heterogeneity and impurities on final product composition. Even the effects of the complex initial composition of this waste flux was addressed by the treatment of about nine tons of Li(0) batteries, allowing a wide proven effectiveness for both process sections. Performing a demonstration campaign with significant amounts of wastes then allowed evaluation of not only the technical feasibility of the process, but also the capacity of the process for producing standardized commercial grade materials despite the heterogeneity of the input materials. Therefore, demonstration of the process confirmed the robustness towards waste variability. In addition, automatic dismantling determined the formation of metal impurity fragments (Fe, Al, Cu) in the electrodic powders. Then, by performing automated opening of batteries and further component separation, the capacity of the process for eliminating such impurities in the final products was also validated.

The quantification of energy consumption in the different sections allowed establishment of a clear distinction between cryo-stabilization and hydrometallurgical product recovery (Libat process), and thermal stabilization and pyro-metallurgical product recovery for Li (Accurec process). In particular, these two options presented almost one order of magnitude difference in their energy consumption, thus determining the consequent environmental impacts.

The economic feasibility of the overall process evidenced the importance of the battery collection system having large amounts of wastes to treat. Alternatively, the integral recycling of batteries can be economically feasible if more types of batteries are treated in the same plant. The demonstration activities evidenced the ability of the cryomechanical section to safely open Li-ion batteries. This is an important added value because, as explained above, the Li-ion battery market and range of applications are far larger than those for Li(0), and they are also expected to grow significantly in the future. Fortunately, lithium-ion batteries are an alternative type which can be treated by the LIBAT process route with only minor adjustments regarding the hydrometallurgical recipes [23]. This would allow faster development of the proposed cryo-mechano-hydrometallurgical route and benefit from the economy of scale law for reducing process costs. In fact, the European market for Li-ion batteries, mainly driven by electric vehicles [24], could grow from around 450 million EUR/year (2017) to 3–14 billion EUR/year (2025). In the long term, the global market could exceed EUR 200 billion EUR/year. To tap into it, Europe would need to further expand its manufacturing base and support the competitiveness of its industry, first of all by ensuring the internal supply of raw materials now completely dependent on non-EU countries. Battery recycling could then represent a contribution to the supply of materials, especially if, not only the more noble metals such as Co, Ni and Cu (obtained

as alloys in the pyro-metallurgical process), but also Li and graphite (which are critical raw materials downcycled in the pyro-metallurgical process), become specific targets of recycling processes.

Even though this process was tested with both Li(0)-MnO₂ and Li-ion batteries, one issue that remains to be further addressed is the possibility of feeding other types of Li primary batteries into the cryomechanical and hydrometallurgical sections. In particular, the thionyl chloride and iron disulfide types were not addressed yet because of complications associated with toxic vapor release and the generation of iron impurities in the leach liquor.

5. Conclusions

In this work, quantitative analysis was performed for an innovative recycling process for Li(0) primary batteries including dismantling, fraction separation, and hydrometallurgical product recovery. This analysis evidenced the technical feasibility of the proposed process in terms of technological readiness and the high quality of the recycled products. Life cycle analysis also quantitatively assessed the environmental advantages of the proposed process in comparison with another innovative process which is based on the pyro-metallurgical route. Economic analysis provided the limits for process profitability, evidencing the importance of improving the collection scheme and using flexible hydrometallurgical processes for implementing at scale and the upcycling of EOL batteries.

Future activities are now in course for a demonstration at pilot scale of the production of Li-ion battery precursors as mixed oxides of nickel, manganese and cobalt (NMC) according to results previously obtained at lab scale [23]. In this case, the cryomechanical section of the LIBAT process will be used for battery opening and component separation, as already done, while the hydrometallurgical section will be specifically dedicated to leaching, purification and NMC recovery within the activities of the LIFE DRONE project [25].

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Appendix A

Table A1. Mass and energy balances for the innovative pyro-metallurgical process developed by Accurec.

Input	Output
Step 1: Thermal pretreatment	
Batteries: 100 kg Electricity: 64.3 kWh	Crack oil: 26.8
Step 2: Mechanical pretreatment	
Pyrolyzed batteries: 73.17 kg Electricity: 41.6 kWh	Steel: 35 kg

Table A1. *Cont.*

Input	Output
Step 3: Lithium thermal recovery	
Black mass: 37.9 kg Bentonite: 0.6 kg Methane: 258.5 Electricity: 158.7 kWh	Gaseous emission: 8.9 kg Lithium carbonate cake: 4 kg
Step 4. Leaching	
Electrode powder: 28.8 kg Sulfuric acid (96%): 41 kg Water: 60 kg Electricity: 11.6 kWh Hydrogen peroxide: 45 kg	Leaching solution: 155 kg
Step 5. Purification	
Leaching solution: 155 kg Sodium hydroxide: 39 kg Electricity: 0.5 kWh	Solid waste: 7 kg
Step 6. Manganese recovery	
Purified solution: 187 kg Sodium hydroxide: 16 kg Electricity: 1.6 kWh	Wastewater: 185 kg Manganese hydroxide cake: 18 kg

Table A2. Costs of raw materials (EUR/kg), utilities (EUR/kWh), and waste treatment (EUR/kg), and the selling prices (EUR/kg) of the products [21,22].

Production Cost		
Raw materials	Sodium carbonate	0.22
	Hydrogen peroxide	1.37
	Sodium hydroxide	0.25
	Sulfuric acid	0.18
	Water	0.0005
	Liquid nitrogen	0.34
Waste treatment	Solid waste treatment	0.64
	Wastewater	0.14
Utility	Electricity	0.27
Selling prices of the products		
Products	Steel scraps	0.18
	Mn hydroxide	0.68
	NMC precursor	22.8
	Graphite	7
	Sodium sulphate	0.1
	Copper scraps	2.6
	Aluminium scraps	0.7
	Lithium carbonate	59

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