

Article

Process Simulation for Li-MnO₂ Primary Battery Recycling: Cryo-Mechanical and Hydrometallurgical Treatments at Pilot Scale

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Abstract: Li primary batteries are currently treated along with other Li batteries in several big pyro-metallurgical plants in Northern EU countries. Nevertheless, pyro-metallurgical processes do not allow for Mn and Li recycling and present negative environmental impacts, on the other hand hydrometallurgical processing can potentially ensure the integral recovery of all materials in Li primary batteries. In this work, preliminary experimental findings obtained in the LIFE-LIBAT project (LIFE16 ENV/IT/000389) are reported. In this project, end of life Li(0)-MnO₂ batteries were cryo-mechanically treated and then the metals were recovered by a hydrometallurgical process. Representative samples of end of life Li(0) batteries were characterized by type and composition. Batteries were stabilized in an N₂ bath and then crushed, sieved, and magnetically separated in the SEVal pilot units. Separated fractions (fine fraction, magnetic coarse fraction, and non-magnetic coarse fraction) were chemically characterized for target metal content (Li and Mn). Fractions were first treated for Li extraction and recovery, then the fine fraction was also leached for Mn recovery. Mass balances evidenced a 55% recycling rate and process simulations outlined profitability in the potentiality range in agreement with battery collection fluxes.

Keywords: Li primary batteries; recycling; pilot scale demonstration; process simulation

1. Introduction

The EU Directive on end of life battery treatment (2006/66/EC) established targets for collection and recycling rates in order to avoid improper disposal, but also to promote resource recovery. In particular, 50% recycling target is fixed for batteries not containing dangerous metals such as Cd and Pb. Nevertheless, the Directive does not include technical aspects concerning the way such end of life devices should be treated in recycling facilities, leaving to the different countries the promotion and adoption of proper collecting schemes and treatment processes. In the same way, no specific obligation was established concerning the target of collection of the different battery types or the recycling rate of specific components, which could be strategic elements or critical raw materials (such as lithium and graphite, respectively) but have little percentage weight in the batteries. Thus, the recycling target can be achieved by treating only certain kinds of batteries (the most abundant on the market) and recycling the components with the highest percentage weight in the wastes (for instance steel and heavy metals).

This has led to the adoption of treatment schemes in which only a partial fraction of the value contained in a battery is recycled and some types of battery with difficult treatment processes are just diluted with other solid charges to solve the problem of their end of life without real valorization of

the components included. This means a “downcycling” of battery components, that is some values are lost and not properly valorized, while the virtuous approach should be “upcycling”, that is not merely recycling the materials, but hopefully giving them additional value (as an example let us consider the production of high value nanomaterials from end of life batteries) [1].

Among the different battery types, Li(0) are primary non rechargeable batteries covering about 3% of primary batteries put on the market, which in turn represents 75% of portable batteries [2]. This means that annually about 2000 ton of this type of battery are put on the market in the EU. Primary Li batteries still present many critical issues regarding recycling. In fact, the presence of highly reactive metallic lithium and flammable organic solvents entail safety risks during the recycling process. As a consequence, Li primary batteries are currently a cost for battery collectors, who after manual sorting of the different battery types, can have revenues from some types (Li-ion batteries), while having to pay for the disposal of some others (Li(0) types).

The most common adopted treatment for Li(0) primary batteries is a pyro-metallurgical one in which whole batteries, or some battery fractions, are smelted along with other solid feeds also from primary sources. This leads to the down-cycling of different battery components such as lithium and manganese, which are lost in the slag. In addition, pyro-metallurgical processes have huge environmental impacts for energy consumption and gas emissions; they can be operated only at large scale to exploit the law of economy of scale to have low production costs; this means that dangerous wastes such as batteries have to travel across EU countries to the few existing pyro-metallurgical plants able to down-cycle them. Apart from this, the pyro-metallurgical processes cannot be the right way to refurbish the battery manufacture system, which the EU is trying to promote with the dedicated initiative of the European Battery Alliance. In fact, in pyro-metallurgical processes, metals are recovered in the reduced metallic form, while metals as oxides are used as electrodic materials in the benchmark technology of batteries, i.e., Li-ion batteries dominating the market for portable electronics and for hybrid and electric vehicles. Using pyro-metallurgy as a treatment option for battery recycling would imply first reducing the metals present in end of life batteries as oxides (with high carbon consumption for such an aim) and then re-oxidizing them to obtain new products for battery manufacture.

Conventional pyro-metallurgical processes do not allow for Li and Mn recycling from Li(0)-MnO₂ batteries because both metals are lost in the slag. An innovative pyro-metallurgical approach has been presented aiming at Li recovery from Li batteries (both Li primary and Li-ion) [3]: in this case, Li was reduced using carbon, volatilized and re-condensed, while Mn in the slag was recovered by leaching.

In the literature, only a few works have been reported regarding the hydrometallurgical treatment of primary lithium batteries and generally including a preliminary thermal treatment for Li oxidation followed by leaching [4,5]. A patent survey also denoted the combined hydro-pyro-metallurgical process of Toxco for Li recycling from Li(0) containing wastes including primary batteries [6]. Nevertheless, to the Authors knowledge no process or plant is now operating in the EU for the dedicated hydrometallurgical treatment of Li(0) primary batteries.

In this context, the LIFE-LIBAT project [7] aims at the demonstration of an innovative cryo-mechano-hydrometallurgical process for the treatment of end of life Li(0)-MnO₂ batteries without preliminary high temperature treatment.

The idea of the project is to demonstrate the technical and economic feasibility of a process able to recycle the different components in these batteries (steel scraps, Mn, and Li) designing and constructing prototypes, which can be used also for the treatment of other types of batteries such as Li-ion batteries [1,8]. The technical solution for the treatment of these batteries includes a cryo-mechanical treatment avoiding the fire and explosion risk due both to residual Li(0) (present in end of life primary batteries for uncomplete discharge) and flammable solvents. In this way, the safe liberation of battery components is achieved and the electrodic materials rich in Li and Mn can be fed to the hydrometallurgical section, where the oxidized products of Mn and Li can be recovered for the manufacture of new electrodic materials.

Environmental benefits generated from the adoption at large scale of hydrometallurgical processes instead of pyro-metallurgical ones will be in terms of the reduction of energy consumption (hydrometallurgical processes are performed in water at temperature lower than 100 °C), the reduction of greenhouse and toxic gas emissions, improved exploitation of resources avoiding down-cycling, and the reduction of potential impacts associated with the transport of dangerous wastes throughout the EU to pyro-metallurgical plants.

In the present work, economic feasibility of the proposed LIBAT process was assessed by process simulations and estimation of economic data.

2. Materials and Methods

Li(0)-MnO₂ batteries collected by SEVal Srl (Colico, Italy) were manually sorted according to the different types as reported in Figure 1. Mechanical treatment was performed on a mixture of cylindrical and prismatic cells (type a and b in Figure 1) and coin cell (type e in Figure 1).



Figure 1. Li(0) primary batteries sorted at the SEVal site: (a) Li//MnO₂ type CR123a (b) Li//MnO₂ type CR2; (c) Li//FeS₂ type AAA; (d) Li//FeS₂ type AA; (e) Li//MnO₂ type coin cell; (f) Li//MnO₂ other formats; (g,h) Li//SOCl₂ in different formats.

Cryo-crushing and hydrometallurgical treatment is performed in the prototypes (potentiality: 50 Kg/d) constructed at the SEVal site including a cryo-mechanical section, a sieving and separation section, a hydrometallurgical section, and a gas treatment section (Figure 2).



Figure 2. LIBAT prototypes at the SEVal site: cryo-mechanical section (yellow), sieving and separation of solid fraction (blue), hydrometallurgical section (orange), gas treatment section (green).

In Table 1, the main characteristic of the equipment included are reported.

Table 1. List of main equipment included in LIBAT prototypes.

Section	Equipment	Operation Description
Cryo-crushing of batteries	Cryogenic tape	Battery cryo-genic pretreatment
	Hammer mill	Crushing of batteries
Separation of solid fractions	Vibrating screen	Electrode powder separation from coarse fraction
	Magnetic separator	Separator of magnetic materials into coarse fraction
Hydrometallurgical operations	Neutralization tanks (3)	Li leaching from separated solid fractions
	Stirred reactor with level, temperature, and pH control	Precipitation of Li as Li_2CO_3
	Filter press	Filtration of Li_2CO_3 product
	Stirred reactor with level, temperature, pH, and pressure control	Mn leaching from electrode powder
	Filter	Removal of electrode powder residue
	Stirred reactor with level, temperature, and pH control	Precipitation of Mn as $\text{Mn}(\text{OH})_2$
	Filter press	Filtration of precipitated $\text{Mn}(\text{OH})_2$
Gas treatment	Bag filter	Dust abatement
	Activated carbon filter	Solvent vapors abatement
	Scrubber	Abatement of dust and acid fumes

During the preliminary activity of the LIBAT project, about 300 Kg of Li(0) batteries were thermally stabilized with liquid N_2 , and then crushed in a vertical axis hammer mill. Crushed samples were then sieved obtaining two fractions identified as the coarse fraction (>1 mm) and fine fraction (≤ 1 mm). The coarse fraction was submitted to magnetic separation obtaining a magnetic coarse fraction (made of steel case) and a non-magnetic coarse fraction (made of internal separators of plastic and paper) Figure 3.

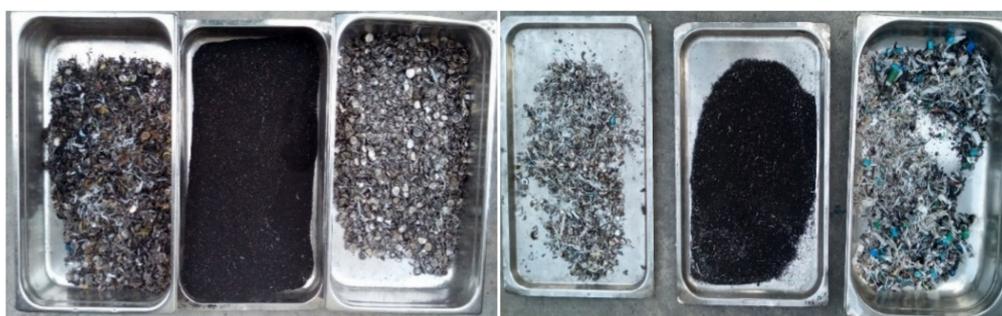


Figure 3. Solid fractions separated from the cryo-mechanical–sieving–separation sequence; from the left to the right: non-magnetic coarse fraction from coin cells, fine fraction from coin cells, magnetic coarse fraction from coin cells; non-magnetic coarse fraction from cylindrical cells, fine fraction from cylindrical cells, magnetic coarse fraction from cylindrical cells.

The LIBAT process includes the hydrometallurgical treatment of solid fractions. In particular, Li extraction from the crushed fractions (fine fraction, magnetic coarse fraction, and non-magnetic

coarse fraction) was performed in a mechanically stirred reactor using water at room temperature with a solid-to-liquid ratio equal to 1:5. After filtration, the liquid stream was recycled for subsequent washing operations of the same fractions thus increasing the Li concentration in solution. The resulting solution was heated at 95 °C and Na_2CO_3 added for the precipitation of Li_2CO_3 [9]. After two hours, the obtained suspension was filtered and oven-dried overnight at 105 °C. The extraction of manganese from the electrodic powder was achieved by leaching for 3 h under stirring at 85 °C with 1:10 g/mL of solid/liquid ratio using 1.3 M sulfuric acid and 20% *v/v* hydrogen peroxide. A manganese-rich solution was recovered after the leachate filtration and used for Mn recovery according to the conditions optimized in [10]: sodium hydroxide was added to the solution obtained from the leaching to increase the pH to around 10; after 2 h, the suspension obtained was filtered and the collected solid oven-dried at 105 °C overnight.

Solid and liquid samples were analyzed by Atomic Absorption Spectrophotometer (AAS, contraAA[®] 300—Analytik Jena AG) equipped with a Xenon short arc lamp as radiation source and with a flame atomizer fed with a mixture of C_2H_2 and air. Multi-standard solution (Merk Millipore 1000 mg/L HNO_3 sol.) was used for calibration and each metal was determined according to a selected wavelength with three replicates for each measurement.

In Figure 4 the block diagram of the process is reported.

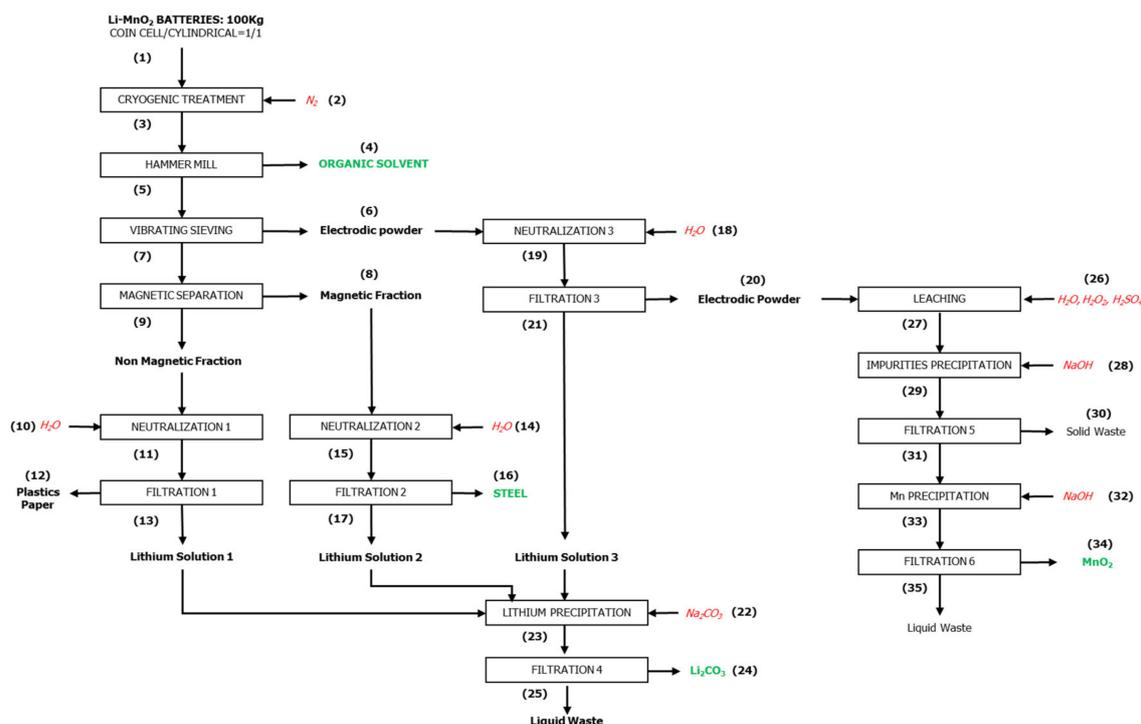


Figure 4. Block diagram for LIBAT process.

At this stage, the hydrometallurgical section was built but not yet in operation. The mass balances for this section were obtained by laboratory scale tests on the solid fractions obtained by cryo-mechanical treatment and separation at pilot scale.

Quantified mass balances including the metal composition of each stream of the process were estimated from pilot scale tests for the cryo-mechanical treatment and fraction separation, and from lab scale tests for the hydrometallurgical section.

These balances were used for preliminary process simulations and the estimation of economic figures assuming the cost and price reported in Table 2 which was fixed according to previous demonstration campaigns.

Table 2. Main economic inputs for costs and revenues used in process simulations.

Stream	Type	Cost/Price (€/Kg)	Description
2	Raw Material	0.25	N ₂
22	Raw Material	0.22	Na ₂ CO ₃
26	Raw Material	0.03684	Leaching chemicals
28	Raw Material	0.92	NaOH
1	Revenue	1	Batteries
16	Revenue	0.2	Steel
24	Revenue	7.7	Li ₂ CO ₃
34	Revenue	10	MnO ₂
25, 35	Wastewaters	0.14	Metal bearing wastewaters

The cost of the LIFE-LIBAT prototype (€320,000) made up of the units reported in Table 1 was used for estimating the plant costs for different potentiality in the process simulation according to a scale law with exponent 0.6.

3. Results

3.1. Sorting and Characterization

Preliminary sorting of the quantity of Li(0) primary batteries denoted that Li-MnO₂ are 49%, Li-SOCl₂ are 45% and Li-FeS₂ only 6%. Target batteries of LIBAT process (Li-MnO₂) are then about half of the total amount of collected batteries in this category.

Considering the Li-MnO₂ type, 53% is made up of cylindrical cells, 42% of coin cells, and the remaining 5% of other formats.

During optimization tests in pilot scale, feeds of coin cells and cylindrical cells were used obtaining solid fractions after sieving and magnetic separation according to the weight distribution reported in the pie chart of Figure 5. Experimental results of separation at pilot scale denoted that electrodic powder represents 52% as weight of the input material for cylindrical cells, while in coin cells this share is 38% due to the reduced size and the relative increase of the external case weight.

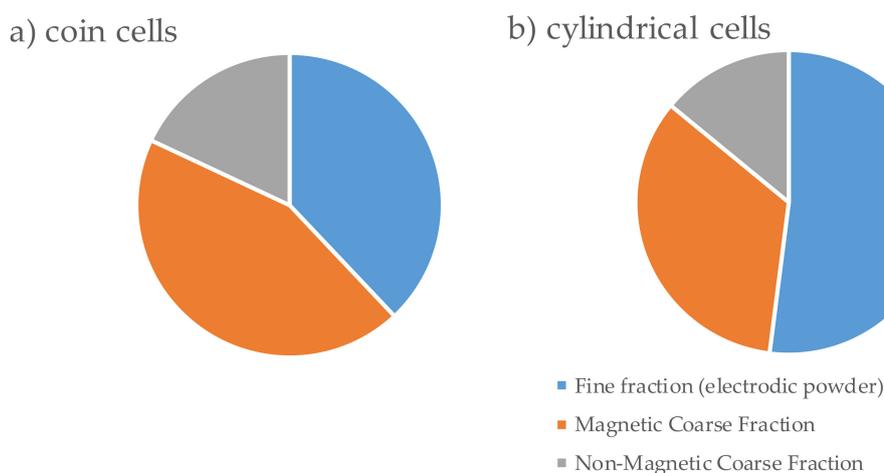


Figure 5. Pie chart for distribution of different waste fractions from cryo-mechanical treatment and separation (sieving and magnetic separation) for coin (subfigure (a)) and cylindrical cells (subfigure (b)).

Chemical compositions in terms of target metal content for the different fractions are reported in Table 3. Chemical characterization of the different fractions denoted that the Mn and Li concentrations

in electrodic powders do not depend on cell format and that the non-magnetic fraction contains residual amounts of Mn and Li.

Table 3. Metal composition ($\text{[mg g}^{-1}\text{]}$) of solid fractions separated from coin cells and cylindrical cells treated in the LIBAT prototype for cryo-crushing and separation.

	Coin Cells		Cylindrical Cells	
	Mn	Li	Mn	Li
Electrode Powder	356 ± 13	39.8 ± 1.2	373 ± 5	39.0 ± 1.4
Magnetic Fraction	6.3 ± 0.5	6.1 ± 5.3	6.4 ± 0.6	0.5 ± 0.4
Non-Magnetic Fraction	290 ± 54	28.9 ± 4.7	79 ± 8	44.5 ± 3.3

In the following, simulations were made according to the weight composition above considering a mixture of batteries made of 50% coin cells and 50% cylindrical cells.

Further details about product characterization can be found elsewhere [9]. In particular, high-purity Li_2CO_3 was obtained by exploiting the solubility gap between the carbonates of Li and Na near the boiling point. XRD characterization denoted the distinct peaks of Li_2CO_3 and solid dissolution denoted a purity higher than 99% with Fe and Mn contents lower than 0.1% [9].

3.2. Quantified Mass Balances of the Process

In Table 4, the quantified mass balances are reported for the complete LIBAT process.

A compact view of mass balances is reported in the Sankey diagram in Figure 6 in which the main inputs and outputs are reported. It should be noted that in this representation wastewaters are all the waters coming out from the different operations that are recycled within the process in the process simulations. The Sankey diagram allowed the direct evaluation of the recycling rate as the sum of the weight of the product as 100 Kg of input wastes are considered in the balances. Then the process in this preliminary version allowed a 55% recycling rate (evaluated as the mass of volatile solvents, steel, Li in Li_2CO_3 , and Mn in MnO_2) which is larger than EU target, and a 70% recovery rate (including thermal valorisation of plastic and paper).

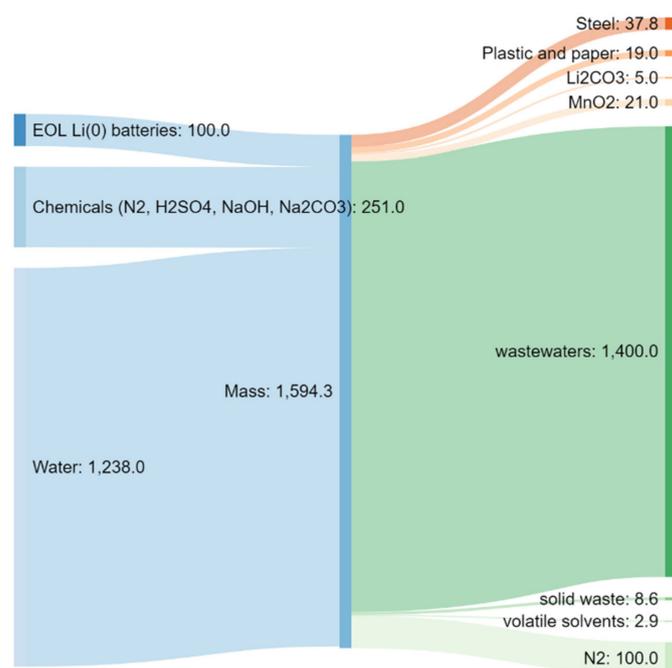


Figure 6. Sankey diagram of the LIFELIBAT process.

Table 4. Cont.

Stream Number	Description of Stream	Li0	Li-Electrolyte	MnO ₂	LiMnO ₂	Li ⁺	Electrolyte-	Organic Salts	Carbon	Volatile Solvents	Steel/Fe0	Plastics Paper	N2	H ₂ O	Mn ²⁺	Fe ²⁺	Impurities Sludge	H ₂ SO ₄ 98%	H ₂ O ₂ 30%	Na ₂ CO ₃	NaOH	Li ₂ CO ₃	MnO ₂	
19	Suspension from neutralization of (6)			11.1	11.9	0.3	4.7	2.6	4.4		1.8			367.7										
20	Electrode powder after neutralization			11.1	11.9				4.4		1.8													
21	Li-bearing solution from neutralization of (6)					0.3	4.7	2.6						367.7										
22	Na ₂ CO ₃ addition for Li ₂ CO ₃ precipitation																			63.6				
23	Li ₂ CO ₃ suspension					1	41.3	11.4						971.2									5	
24	Li ₂ CO ₃																						5	
25	Waste waters after Li recovery		0				41.3	11.4						971						27				
26	Leach liquor for Mn extraction													267				25.8	40					
27	Suspension after Mn leaching					0.9		2.6	4.4					267	13.3	1.8		25.8	40					
28	NaOH for impurities precipitation																					2.1		
29	Suspension after precipitation					0.9		2.6	4.4					267	13.3		3	25.8	40					
30	Solid waste			0.6	0.6				4.4															
31	Mn-bearing solution					0.9		2.6						267	13.3			25.8	40					
32	NaOH for MnO ₂ precipitation																					19.7		
33	MnO ₂ suspension					0.9		2.6							0.1									21.3
34	MnO ₂																							21.3
35	Waste water after Mn recovery					0.9		2.6						267	0.1			25.8	40		12			

As for energy balance, a preliminary estimate was made for the LIBAT process related to the treatment of 100 Kg of batteries taking into consideration the nominal power consumed by the equipment. The following contributions were estimated: cryogenic crushing and separation (15 KWh), Li recovery (5 KWh), and Mn recovery (25 KWh).

As for energy consumption, a preliminary comparison with the pyro-metallurgical process was elaborated considering the pyro-metallurgical process including Li reduction, vaporization, and re-condensation, being the only one allowing Li recovery [1]. For the comparison it was assumed that batteries were preliminary cryo-crushed and separated and then, only the fine fraction fed to the furnace for Li reduction, volatilization, and condensation, while Mn is recovered from the slag by leaching and precipitation as in the LIBAT process. Pyro-metallurgical operations for Li recovery determined an energy consumption of 18 KWh. This means that using the pyro-metallurgical operation for Li recovery required an extra energy consumption of 13 KWh.

This preliminary estimate will be further tuned after demonstration activities.

3.3. Process Simulations

Process simulations in the LIBAT prototype were performed considering the following scheduling of the operations for completing the treatment of one batch (900 Kg of batteries):

- 9 cycles for crusher, vibrating sieve, and magnetic separator
- 9 cycles for neutralization 1
- 1 cycle for neutralization 2
- 3 cycles for neutralization 3
- 10 cycles for leaching/precipitation of impurities
- 10 cycles for precipitation of the Mn
- 1 cycle for lithium precipitation

The number of cycles was established to be in line with the sizes of the reactors and filter presses available for each operation and to allow the various neutralization operations to reach the concentration of lithium suitable for the subsequent precipitation reaction of lithium carbonate. On the basis of the duration of each operation, it was possible to schedule all the operations of the process with an overall time of 46.5 h per batch. This entails the possibility of carrying out 202 batches per year for a total of 182 t/year of batteries to be treated. Process simulations were also performed increasing the potentiality (two and five times) considering the treatment of 900, 1800, and 4500 Kg/batch and then a plant potentiality of 364 and 909 t/y. These values were chosen considering that the total amount of this type of battery collected in the EU is about 2000 t/y with about 300–500 t/y collected in Italy. Then the low and intermediate scenarios include the treatment of Italian batteries while the largest scenario includes the option of collecting batteries also from other EU countries. Plant costs for increased potentiality were estimated assuming 0.6 power scale law starting from a plant cost of LIBAT prototype (€320,000). In Table 5 the economic evaluation report for the different potentialities is reported. Process simulations denoted a payback time of 5.3 year for the lowest potentiality, decreasing to 3.8 and 2.5 years for the intermediate and largest potentiality, respectively.

Table 5. Economic evaluation report for the different potentialities.

Potentiality (t/y)	182	364	909
Total Capital Investment (€)	538,000	815,000	1,412,000
Operating costs (€/y)	308,000	594,000	1,457,000
Total revenues (€/y)	477,000	955,000	2,387,000
Gross Margin (%)	35.39	37.81	38.95
Return on the investment (%)	18.86	26.59	39.5
Payback time (y)	5.3	3.8	2.5

The cost breakdown for operating costs are reported in Table 6 evidencing that the main contributions are for labor dependent cost (41–42%) followed by costs related to waste treatment (28–29%) and to raw materials (25–26%).

Table 6. Operating cost breakdown for the different potentialities.

Potentiality (t/y)	182	364	909
raw materials (€)	77,000	155,000	386,000
labor dependent cost (€)	126,000	247,000	619,000
waste treatment (€)	85,000	170,000	426,000
utilities (€)	20,000	21,000	26,000
TOT (€)	308,000	594,000	1,457,000

4. Discussion

Preliminary process simulations performed using material balances from pilot and lab scale denoted that economic feasibility can be achieved in the range of potentiality of Li(0) batteries actually collected in Italy. Finalization of mass balances in the pilot scale and further process optimization will be performed during the next activities of the LIFE-LIBAT project.

The proposed process is an alternative to downcycling pyro-metallurgical plants allowing the recycling of potentially all materials included in these batteries. Preliminary tests at pilot scale demonstrate the technical feasibility of cryo-crushing giving the separation of directly recoverable steel from the external case and electrodic powder. This powder is then treated for Li and Mn recovery at lab scale and further tests are planned at pilot scale.

Some additional aspects should be considered regarding the flexibility of the proposed process and plant for treating other types of batteries. In particular, considering primary Li batteries, the Li-MnO₂ type is about 50% of the total collected batteries of this specific type. The other 50% is mainly Li-SOCl₂ presenting problems regarding the toxicity and corrosion of SOCl₂ and its decomposition products (SO₂). A campaign will be dedicated to Li-SOCl₂ batteries in the demonstration activities of the LIFELIBAT project in order to assess the technical feasibility of the cryo-mechanical treatment and the gas treatment section for treating this specific type of Li(0).

More interestingly the proposed process (cryo-mechanical and hydrometallurgical treatment) will allow the treatment of Li-ion batteries, which are rechargeable batteries used in almost all electronic devices (laptop, smartphone, tables) and hybrid and electric vehicles. In addition during the project, a campaign dedicated to Li-ion batteries will be performed to assess the flexibility of the process for this type of battery. This could be a crucial aspect for further exploitation of the process. In fact, Li-ion batteries are largely diffused (about 75,000 t were put on the market in EU countries in 2015 [11]) and contain also critical raw materials such as Co increasing the recoverable value from these wastes. Then, the possibility of treating Li-ion batteries according to the proposed route will dramatically change the scale of operation of the process and thus improve its economic feasibility.

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