Metal Recovery from Spent Lithium-ion Batteries by Hydrometallurgy

Francisco Veiga
francisco.j.m.veiga@tecnico.ulisboa.pt

Instituto Superior Técnico, Lisboa, Portugal
October 2021

Abstract

Given the current energy transition, the battery market is in a state of rapid growth. Consequently, in the near future, an exponential increase in the number of end-of-life batteries is expected. Bearing in mind the environmental problems after end-of-use and the criticality of resources, the recycling of valuable metals from spent batteries is of the utmost importance. Herein, the processes of foil and powder separation and leaching are researched with the aim of suggesting a process that can be implemented industrially. Two foil and powder separation methods were tested: calcination and solvent dissolution with N-Methyl-2-pyrrolidone (NMP). The electrodes were successfully calcinated at 400ºC for 5 hours, with 100% disaggregation. Subsequently, the effect of calcination on the leaching yield was also studied, supporting the previous result. Prior to the factorial design experiments, the influence of reducer on the leaching behaviour was also conducted, introducing the possibility of electrode foils as potential reducing agents, and setting $Na_2S_2O_5$ as the leading reducer.

The optimal leaching conditions were found to be 3 M of H_2SO_4 as leaching agent, 0.25 M of $Na_2S_2O_5$ as reducing agent, an L/S of 5 L/kg, temperature of 80ºC, for 30 minutes. For the aforementioned parameters, the overall recovery in the leaching solution for Li, Ni, Mn, Co, Cu, and Al was 95.03%, 99.55%, 99.99%, 97.60%, 100%, and 72.47%, respectively. Additionally, an introduction to the metal separation process was also made.

Keywords: Lithium-ion Battery, Hydrometallurgy, Inorganic Acid Leaching, $Na_2S_2O_5$, Separation, Extraction.

1. Introduction

The world is currently facing a massive migration from fossil fuel to electric energy, a transition to a low-carbon economy, due to global warming, and the upcoming energy crisis. And so, as stated by the European Technology and Innovation Platform on Batteries, "(…) within this decade, where it is technologically and economically viable, everything that can be electrified will be electrified" [1].

The European Commission has established the objective of reducing Greenhouse Gas (GHG) emissions by 80% to 95% by 2050 when compared to 1990. This low-emission strategy has resulted in a growing switch from the traditional Internal Combustion Engines (ICEs) to Electrical Vehicles (EVs) [2,3].

This continuous conversion of ICEs into EVs has been increasing the need for electrochemical energy storage devices, i.e. batteries, with Lithium-ion Batteries (LIBs) being recognised as the preferred choice [3–5].

When the LIB reaches the design lifetime, generally 8-10 years for EVs, the battery must be replaced, and to create a true Circular Economy (CE) for LIBs, disposal must be avoided, reducing dependence from countries with geopolitical conflicts and tackling the issue of availability of critical raw materials, e.g. cobalt, lithium, and graphite. Also, landfilling can constitute threats to human health and the environment, in terms of explosions, leakages of hazardous elements, especially with the expected end-of-life (EoL) LIB quantity increase in the upcoming future. [4–6].

After reflecting on the information mentioned above, it is obvious that efforts to improve the recyclability of spent batteries are necessary. This work intents to make a contribution for that need. At present, the two main methods applied for recycling of spent LIBs are hydrometallurgy and pyrometallurgy, with the main difference between them being the metal-extraction process. This work, integrated into the project Baterias 2030 – Batteries as a Central Element for Urban Sustainability,

1

focuses on recovering elements from two Nickel Manganese Cobalt (NMC) spent LIBs from an EV by hydrometallurgy, since this is a simpler and environmentally friendlier process, with lower energy requirements and higher purity [5].

2. Background

The recycling process can be divided into two parts: pre-treatment and metal extraction. In the following sub-chapters, descriptions of different alternatives for each step can be found.

2.1. Pre-treatment

As spent LIBs have a small amount of remaining charge, they can detonate during the recycling process. And so, the first step is the discharge of the LIB, preventing short circuits and self-igniting. Two common methods used to neutralize LIB's charge are either heating up to 300ºC or soaking the spent LIBs in NaCl or Na_2SO_4 saturated solution for 24 – 48 hours. [4,7,8].

After discharging, the spent battery packs are dismantled, often manually (due to the LIB's wide variety of physical configurations), allowing the separation and recovering of the metal casings, electronic devices, cables, and other components. Following dismantling, there is mechanical separation, the most used technique at industrial level, which has the sole function of removing the outer case, to segregate valuable materials, and reduce scrap volume. This technique includes crushing, magnetic separation, sieving, grinding by milling, and other physical separation operations. [4,7,8].

The last step on the pre-treatment procedure chain is the separation of the cathode materials from the foil. Some of the most common methods are thermal treatment, ultrasonic separation, and solvent dissolution method. Solvent dissolution methods use organic solvents with good solubility, e.g. NMP, DMF, DMAC, DMSO, to weaken the adhesion force between the foils and activate materials. The ultrasonic operation, due to the effect of cavitation, is recognized as an effective method for separating cathode materials from foil substrates. Finally, the thermal methods eliminate the adhesive force between the binder and the cathode active material using high temperatures (400 – 700ºC). In addition, the high temperatures induce metals phase transformation, increasing the subsequent leaching efficiency. [4,7–10].

2.2. Metal Recovery Processes

The objective of the metal extraction process, as the name suggests, is to convert the metals, usually in the cathode materials, into an alloy form or a solution state to promote separation. There are various metal recovery methods currently employed, e.g. pyrometallurgical or hydrometallurgical processes, direct regeneration, or a combined pyro/hydrometallurgical process. This work uses hydrometallurgy as its metal recovery process [4,6,11].

Hydrometallurgical processes involve dissolving the cathode materials with proper chemical reagents, i.e. leachants, and separating the metals in the leaching solution. Contrary to pyrometallurgical processes, hydrometallurgical processes require processing after discharging and dismantling to maximize the recovery rate. The core operation is the leaching where the electrode fraction of the spent LIB batteries is reacted to form aqueous soluble ions. Depending on the employed solution, the leaching operation can be classified as acid leaching (inorganic or organic), alkaline or ammonia leaching, electrochemical leaching, and bioleaching. Additionally, reducing agents are usually used to reduce the transition metal oxides to lower oxidation states, facilitating their dissolution in the acid solution, and, therefore, improving the leaching efficiency. [5,7,11,12].

Temperature, acid and reducing agent concentration, reaction time, and pulp density are the main parameters of this process.

The procedure is usually carried out at a temperature below 100ºC, reducing energy costs. The valuable metals present in spent LIBs are dissolved in the leaching solution and therefore separated from the undissolved residues by filtration. From this leaching liquor metals are reclaimed by several approaches, including: chemical precipitation, solvent extraction, ion exchange, etc. Because impurities such as aluminium, magnesium, calcium, and iron are also leached, additional purification and separation processes are required [4,5,7,11,13,14].

Chemical precipitation, one of the most traditional, simple, and practicable separation technologies, uses a variety of chemical reagents, i.e. precipitants, and depends on the different solubilities of metal compounds at defined pH values. Here, precipitants are added into the leaching solution and their anions will bond the metal cations, forming insoluble precipitants [14–16].

In solvent extraction, the extraction system is formed by extractants, one or more types of organic chemicals with specific functional groups, mixed with specific diluent and modification reagents. The process consists of two operations: extraction and stripping. In extraction, the metals in the aqueous phase, i.e. leaching liquor, are transferred to the

organic phase, where the metals are more soluble. Following extraction, the extracted metals are recovered from the organic phase to the stripping solution. For cases where the solution contains multiple metal ions, more than one extractant is commonly employed in order to secure a higher selectivity [14,15,17].

The main advantage of the hydrometallurgical process is the possibility of producing new battery precursors from the waste with sufficient purity. It is also more versatile regarding the variation of the feed materials resulting from the evolution of the cathode chemistries. Despite the large demand for chemical reagents, the possibility of extended use for several years of the chemical reagents and the possibility of re-utilization of several by-products within the same technology, make it possible for minimization of the overall secondary waste generation. Nevertheless, the wastewater produced has negative environmental impacts, if not treated. Having said this, hydrometallurgy seems to be one of the most promising approaches to meet the requirements, but also to create a path to a circular economy in the battery market [4,5].

3. Experimental Methodology

3.1. Material

The spent LIB packs were provided by Valorcar and discharged and dismantled in Ambigroup and Palmiresíduos, two recycling plants in Portugal, in light of the project a Study Strategy for Treating Lithium-ion Batteries.

All of the chemicals used in this work were of p.a. purity and were kindly supported by Laboratório Nacional de Energia e Geologia (LNEG), where all of the experimental procedures were developed.

3.2. Pre-treatment

This first stage has the function of removing the binder and, consequently, allowing the separation of the electrode active material from the foil. A crucial step in order to maximize efficiency in the leaching process.

3.2.1. Thermal Treatment

This stage starts by cutting small squares from the cathode and anode with approximate dimensions of 3.5 x 3.5 cm, which are then weighed and placed in crucibles to be thermally treated in a *Carbolite* muffle. Two temperatures were studied, namely 400ºC and 500ºC, for 1 and 5 hours. Here, the cathodes and anodes from each cell were tested separately.

3.2.2. Dissolution Process

Similar to the beginning of the thermal treatment, the electrodes are cut into small squares and weighed. After that, a certain volume of N-methyl-2-pyrrolidone (NMP) was measured and mixed with the cut electrode squares in a round glass reactor with cover. As in He's work [18], the solid/liquid ratio used was 1:10 g/mL. The glass reactor was inserted in a temperature-controlled oven from *Cassel* with orbital agitation (120 rpm) for a specific amount of time. The temperatures studied were 25ºC and 90ºC, for 1 and 2 hours. Afterwards, the solution was filtered, and the filtered solids (active material) were dried in an oven at 55ºC. Along with these studies, another dissolution process was done using an ultrasonic bath from *Fritsch Laborette* at room temperature for 1 hour.

In every experiment, the cathodes and anodes from each cell were treated separately.

3.2.3. Mechanical Treatment

After evaporating the PVDF binder, two different mechanical treatments were done: manual brushing and crushing.

3.3. Characterization

Samples were characterized using Inductively Coupled Plasma-Atomic Emission Spectometry (ICP), Atomic Absorption Spectrometry (AAS), Scanning Electron Microscopy (SEM), Field Emission Gun Scanning Electron Microscope (FEG-SEM), with Energy Dispersive Spectroscopy (EDS), and X-Ray Powder Diffraction (XRPD).

3.4. Acid Leaching

The acid leaching experiments can be divided into three parts. The first one, where the influence of the thermal treatment conditions in the leaching efficiency was studied. A second one, where the reducing behaviour of both electrode foils, was, independently and simultaneously, investigated. And, lastly, a third one, where the variation of four different factors was explored.

The effects of four different factors on Co, Ni, Li, and Mn leaching efficiency were investigated using a Factorial Design Experiment (FDE) methodology. The studied parameters were acid concentration, temperature, time, and liquid/solid ratio (L/S). The chosen leaching and reducing agents were H_2SO_4 and $Na_2S_2O_5$, respectively.

For the two first sets of experiments, the cathodic powder was obtained from the manual brushing step. In the last experiment, the cathode powder came from the grinding of the two different cells electrodes. Sampling was carried out using a Jones

riffle splitter from *Minerais & Métaux*, and a *Spinning Riffler* from *Microscal Ltd*.

Experiments were done using round glass reactors put in a temperature-controlled oven from *Cassel* with orbital agitation (120 rpm) for a specific amount of time.

3.5. Metal Separation

Solvent extraction was used for separating Cu from the leaching solution. The extractant used was composed of a 20% v/v of ACORGA M5640 diluted in ESCAID 102. The Cu was stripped from the organic phase using a solution of 3 M H_2SO_4. The resulting aqueous solution, loaded with Cu, was evaporated until crystallization of $CuSO_4$ occurred. The crystallized Cu was then filtered, washed with acetone, and dried in an oven at 55ºC for 24h.

Al, Co, Mn, and Ni were separated using chemical precipitation. To adjust the pH value (measured with a glass combined electrode connected in a pH meter by *Hanna Instruments*) the precipitant used was a solution of 4M of NaOH. The neutralization and precipitation was carried out at room temperature in a glass cylindrical reactor with an overhead stirrer provided with a two-blade impeller. The obtained precipitates were filtered, washed with demineralized water, and dried in an oven at 55ºC for 24 hours.

To end, the resulting Li-rich solution was evaporated in a hotplate and then a solution of 2.5 M sodium carbonate (Na_2CO_3) was added to precipitate Li_2CO_3. The precipitate attained at this stage was too filtered, washed with a saturated solution of Li_2CO_3, and dried in an oven at 55ºC for 24h.

4. Results
4.1. Pre-Treatment
4.1.1. Thermal Treatment

Figure 1 summarizes the weight loss throughout the process. It is possible to observe a tendency for an increase in weight loss with the increase in temperature and exposure time. This said the same is not true for cell 7 at 400ºC. One explanation for this phenomenon is that the binder can reach its removal maximum after 1 hour at 400ºC, thus not showing any weight loss after 5 hours.
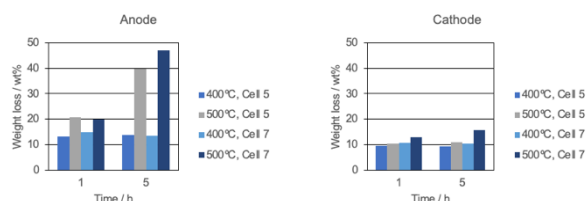

Figure 1 - Weight loss of electrodes over time during calcination.

For both electrodes, 500ºC for 5 hours registers the highest weight loss, as expected. The high weight losses in the anodes might be linked to the partial decomposition of the graphite.

The anode foils turn extremely brittle after the calcination treatment. This sudden change of behaviour from the material might be justified by the occurrence of Cu oxides on the surface of the electrode material during calcination. As stated by Cástrejon-Sánchez et al. [19], for temperatures above 400ºC, calcination promotes the growth of a passivating copper oxide layer composed of Melaconite (CuO) and Cuprite (Cu_2O). This hypothises was supported by SEM and XRPD.

The cathode electrodes presented, with the exception of the cathode from cell 5 at 400ºC for 1 hour, maximum disaggregation in every temperature and exposure time, by manual brushing, revealing an acceptable decomposition of the binder material. The disaggregation of graphite from the anode electrodes was impossible to be studied due to the disaggregation of the supporting copper foils.

These results made it possible to determine the percentage of cathode powder and foil for each cell. On average, cell 5 is composed of 9.57 ± 0.22 % foil and 90.43 ± 0.22 % powder and cell 7 of 16.65 ± 0.59 % foil and 83.35 ± 0.59 % powder. These results can be compared with the aluminium content determined by chemical analysis of the electrodes, assuming that the aluminium present is only coming from the foils. The values are 6.9 and 9.6%, for cell 5, and 17.8 and 16.7% for cell 7, although not being exactly the same, they are in the same order of magnitude.

4.1.2. Solvent Dissolution

Here, the PDVF removal process was performed using an organic solvent, NMP. The results for cathode disaggregation are disclosed in Figure 2 and contemplate the cathode powder obtained during manual brushing and filtration of the NMP.

In the tests varying temperature, cell 7 presents a predictable course, increasing disaggregation with the increase of time and temperature. Cell 5, on the other hand, reveals the opposite, with disaggregation reaching its peak, approximately 39%, at the first stage, 25ºC after 1 hour.

The results for anode disaggregation are not displayed here seeing as they were all inferior to 0.5%.

The majority of the electrode powder detached during solvent dissolution is released into the solvent. As the electrode powder is ultra-fine, the filtration process became difficult and with some losses.

After careful consideration, bearing in mind the disconnection between the poor disaggregation results and the losses during the filtering process, the pre-treatment selected for the subsequent leaching study operation was the thermal treatment.
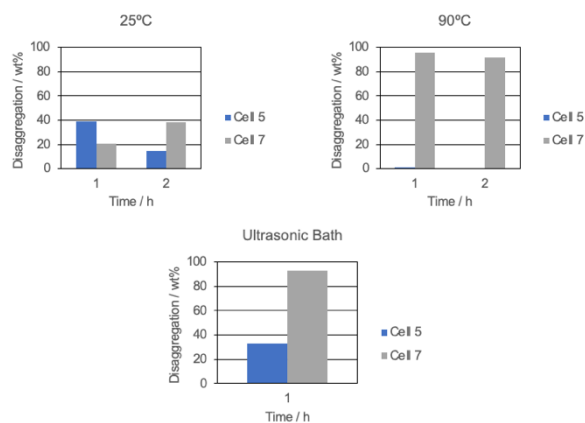

Figure 2 - Percentage of black mass detached from the cathode foils after solvent dissolution.

4.2. Impact of calcination in the leaching behaviour

The powder obtained in each thermal treatment, i.e. detached from the foil, was leached with 2M H_2SO_4, 0.25 M $Na_2S_2O_5$, at 60ºC, 120 rpm, and with a L/S ratio of 5 L/kg, for 2 hours. The leaching yield results are presented in Figure 3.

The first observation is that the reaction is fast and at the time of the first sample, 30 minutes, the results are very close to those obtained at the end of the leaching experiment, with some subtle differences.

As an ion with higher mobility, Li is more easily removed from the solid structure and therefore has the highest leaching yields of all the metals at each time in both cells. Electrolyte salts, if any, might also be contributing to the high leaching yields due to their high solubility. Al, being a contaminant, if present would be at small yields, which is the case (less than 1%).

400ºC for 1 hour is the condition that presents the worst results for cell 5. 500ºC for 30 minutes presents the worst leaching yields for cell 7, and for cell 5 the results are also lower than for 5 hours at both temperatures. This, allied to the fact that, as previously stated, at higher temperatures for longer periods the calcinated anode samples start to oxidize, hampering the separation of the powder from the foil and contaminating it with Cu, calcination at 400ºC for 5 hours was the pre-treatment selected for the subsequent leaching experiments.
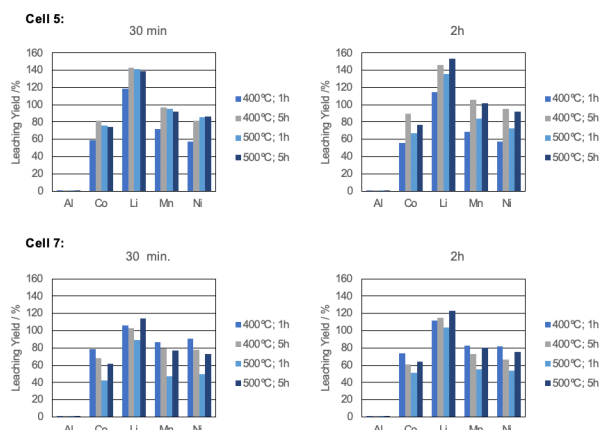

Figure 3 - Leaching yield of each metal from the calcinated cathode powder using 2M H_2SO_4, 0.25 M $Na_2S_2O_5$, at 60ºC, L/S=5 L/kg, and 120 rpm, during 30 minutes or 2 hours of leaching.

4.3. Impact of the presence of reducer in the leaching behaviour

The reducers tested were $Na_2S_2O_5$, Al foil, and Cu foil. The idea behind these tests was to evaluate if the foils can (or not) have a reductive effect in the leaching of the metals from the cathode. Six different leaching tests were done on a detached cathode powder sample after calcination at 400ºC for 5 hours of each cell. The L/S ratio was set at 5 L/kg, the leaching temperature at 60ºC, the $Na_2S_2O_5$ concentration at 0.25 M, and the H_2SO_4 concentration at 2M. The amount of added electrode foil (when applicable) was proportional to the quantity of electrode powder, i.e. the foil/powder ratio was 2/8 and 1/9 for cells 7 and 5, respectively.

As in the previous set of experiments, the first sample results show that the reaction is quick, achieving leaching yield values close to the ones obtained at the end of the process. Li continues being the metal with the highest leaching yield, for the same reason as before, being an ion with higher mobility, less bound to the solid structure.

A test using only an acid solution was carried out to evaluate the absence of reducer. Figure 4 reveals that the absence of a reducing agent suppresses the leaching yield results, with the exception of Li, for the same reason given above and because it doesn't change its oxidation state during leaching.

Higher leaching yield values are achieved when using $Na_2S_2O_5$, or a combination of $Na_2S_2O_5$ with the electrode foils. For the second case, the yield increases with time probably because the pulp density increases, due to the presence of the cut electrode foils, and the acid takes more time to take effect.

For cell 5, the worst results were obtained when Cu foil was used as a reducer. Al foil's performance

as a reducing agent was more acceptable, revealing increases in the leaching yields, especially in the first 30 minutes, but still inferior to the ones using $Na_2S_2O_5$. This yield gap between Al and Cu wasn't as pronounced for cell 7. This said, $Na_2S_2O_5$ still maintains its role as a leading reducer.
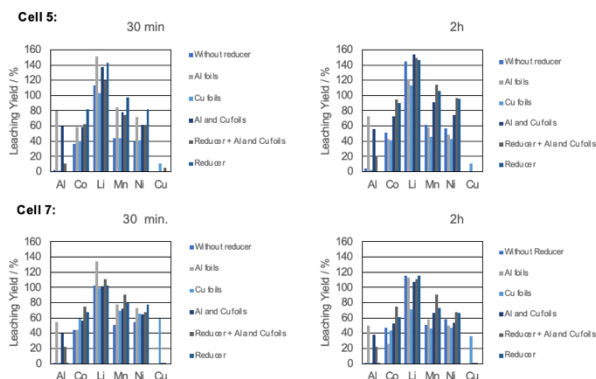

Figure 4 - Leaching yield results of each metal with the different leaching parameters.

4.4. Optimisation of the leaching operation

For the optimisation of the leaching operation, the material used should be as similar as possible to a real fraction of black mass in industrial practice. With the intention of simulating a process of industrial crushing, a mixture of both cells was prepared in the corresponding proportions, i.e. 66.18% of cell 5 and 33.82% of cell 7.

4.4.1. Material Preparation

After selecting the more effective pre-treatment, a considerable amount of electrode material was calcinated at 400ºC for 5 hours and crushed in a cutting mill with a discharge grid of 6 mm. This material is designated as "pre-treated". As means of comparing, a weighed amount of non-treated material was also crushed.

Following crushing, the resulted material underwent granulometric distribution using a normalized series of sieves at a ratio of square root of 2.

After crushing the first time, the majority of electrode foils that showed signs of disaggregation were cathode foils (aluminium), present in the coarse fractions. By the contrary, the evidence of presence of clean anode foils (copper) was scarce. And so, a second crushing step was introduced for the coarser material, i.e. with a grain size superior to 0.5 mm, in order to increase disaggregation of graphite from the anode foils. In this second step, the same mill was used but with a discharge grid of 2 mm. As in after the first crushing, the resulting material underwent granulometric distribution using the same fifteen meshes.

The resulting cumulative curves for both pre-treated and non-treated samples are displayed in Figure 5. The first conclusion is that the pre-treatment facilitated the disaggregation of the electrode powders. Additionally, it is possible to see that, from the first crushing, more than 20% of the powder is thinner than 0.045 mm, revealing a satisfactory electrode powder release. On the contrary, for the non-treated fraction of material, less than 1% of the powder is thinner than 0.045 mm. Meaning that for the pre-treated sample there is more powder disaggregation, thus emphasizing the importance of the binder removal role in the disaggregation process.
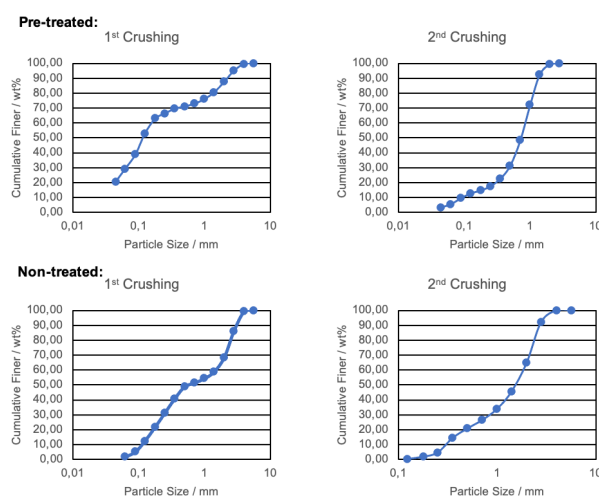

Figure 5 - Cumulative curves for pre-treated and non-treated material after the first and second crushing.

The larger sieved particles from the first crushing (particle size superior to 0.5 mm) were crushed one more time. 0.5 mm was chosen as the parting sieve because thenceforth, little to no aluminium particles were seen in the sieved content. To validate this choice, the sieved content of a selected group of sieved material samples was dissolved with aqua regia and analysed with AAS. The results are available in Figure 6.

Figure 6 confirms the theory introduced above that the second crushing would allow the disaggregation of the graphite, whereas the cathode powder would be abundant in the material resulting from the first crushing. And so, although some contamination from Cu and Al may occur from the second crushing, it is worth it, seeing as contaminants may be extracted through extraction processes, and another crushing step allows for the disaggregation of graphite and more cathode elements. This cathode elements disaggregation may appear small on a laboratory scale but, on a large scale, it can represent a great deal of material.

In the results for the second crushing of the non-treated material, there is still a considerable amount of cathode material present, which is normal considering that there isn't as much disaggregation from the electrode foils.
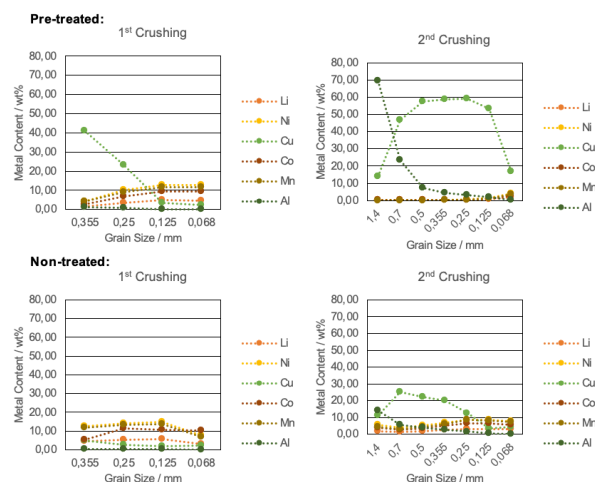

Figure 6 - Metal content in some selected sieved material fractions after first and second crushing, for pre-treated and non-treated material.

Finally, regarding the choice of the parting sieve, the results from Figure 6 confirm, for both pre-treated and non-tread materials, the higher concentration of electrode powder material, making 0.5 mm an acceptable choice.

4.4.2. Factorial Design Experiment

To evaluate the significance of the main factors in the leaching yields, an FDE was done. The adopted ranges for the parameters were as follows: 60 and 80ºC for temperature; 5 and 7.5 L/kg for L/S; 2 and 3 M for acid concentration; and 30 and 120 min for time. The other processing conditions were maintained constant, namely the concentration of the reducing agent ($[Na_2SO_4]$ = 0.25 M) and the stirring velocity (v = 120 rpm). Table 1 summarizes the FDE's factors and levels, along with the leaching yield for each individual metal. Tests 1 to 16 correspond to the combination of factors while tests 17 to 20 are replicates at the central point of the programme, through which the experimental error can be estimated.

By applying Fisher's distribution, the quantification of the significance of the effects can be studied through the analysis of the variance.

In general, the concentration of leachant and temperature have a positive and significant effect on the leaching efficiency, i.e. have a p-value inferior to 0.05, with Ni at the limit of significance. Exceptionally, for Li the concentration of the leaching has a very significant effect, i.e. the p-

value, in this case, is inferior to 0.01. On average, the leaching yields rise by about 25% and 10% when the concentrations of leaching agent and temperature increase, respectively. For Al temperature has no significant effect.

Table 1 - List of experiments and corresponding responses obtained in the 2^4 factorial design.

Exp.	Factors and levels				Leaching Yield / %					
	L/S	[H₂SO₄]	T	t	Li	Ni	Mn	Co	Al	Cu
	L/kg	M	ºC	min						
1	5	2	60	30	74.2	63.7	70.3	63.9	18.0	70.1
2	7.5	2	60	30	83.8	75.2	77.4	75.6	47.0	62.7
3	5	3	60	30	95.2	86.3	93.9	87.5	78.8	85.6
4	7.5	3	60	30	93.0	87.0	85.9	85.7	89.5	64.9
5	5	2	80	30	88.2	83.2	89.7	87.1	14.7	82.7
6	7.5	2	80	30	84.8	75.9	78.2	79.2	58.0	63.3
7	5	3	80	30	95.0	99.6	100.0	97.6	72.5	100.1
8	7.5	3	80	30	102.4	102.9	101.8	104.4	103.4	78.0
9	5	2	60	120	68.8	65.2	66.9	67.0	19.6	70.4
10	7.5	2	60	120	77.2	69.2	73.4	71.9	47.6	62.5
11	5	3	60	120	97.6	89.6	98.0	93.2	84.7	91.4
12	7.5	3	60	120	93.0	81.6	83.9	82.3	92.2	69.3
13	5	2	80	120	87.9	78.6	88.1	81.4	41.7	79.4
14	7.5	2	80	120	75.5	64.3	67.0	65.8	49.7	62.8
15	5	3	80	120	95.6	92.5	97.0	93.7	75.2	102.5
16	7.5	3	80	120	113.7	104.5	110.0	106.1	112.6	103.4
17	6.25	2.5	70	75	99.6	102.6	110.2	102.3	72.0	76.4
18	6.25	2.5	70	75	106.8	108.0	101.0	86.1	88.0	90.9
19	6.25	2.5	70	75	103.1	93.4	96.1	100.2	79.7	80.5
20	6.25	2.5	70	75	105.7	107.3	103.7	96.9	96.7	82.4

The L/S ratio seems to not have any significant effect on the leaching efficiency of any metal besides Al and Cu. For Al, the ratio is significant and positive, with the leaching yield increasing by about 24% with the increase of L/S. On the other hand, for Cu the ratio has a negative and significant effect, meaning that the leaching yield decreases by about 14% when the L/S increases. This may be due to the fact that with higher L/S values, there is more volume and more reducer available for the reaction which may hinder the dissolution of Cu but increase the dissolution of Al.

As a final point, taking into account all the effects described above, experiments 7 and 8 create the optimal conditions for the leaching process. Seeing as the yielding results are very similar between experiments, and experiment 8 has a higher L/S, experiment 7 is the chosen one.

To support this claim, XRPD was performed in the final leaching residue. The diffractogram reveals a pronounced presence of graphite with very small peaks of cryolithionite ($Na_3Li_3(AlF_6)_2$), supporting the leaching yield results for experiment 7. Although Al yield was not complete, that did not significantly affect the composition of the graphite leach residue, since the initial Al content in the material was low (approximately 1.2 wt%) due to efficient separation of Al foil resulting from the crushing and sieving procedure applied.

4.5. Metal Separation

The bulk solution used in the following separation processes was a mixture of every leaching liquor resulting from the previous FDE.

4.5.1. Cu Extraction

Before starting the extraction process, the pH of the solution was raised to 1.59 by adding of 57 mL of a 4 M NaOH to 150 ml of the mixture leaching solution. 150 mL of the pH-corrected solution was used in the subsequent extraction process.

Solvent extraction involves two operations: extraction and stripping. For the first operation, 150 mL of ACORGA M5640 was used. Following extraction, the organic phase was stripped of all Cu using 150 mL of a 3M H_2SO_4 solution, to guarantee maximum Cu recovery. A sample of each stripping solution was diluted and analysed with AAS.

The yield for the complete extraction circuit, extraction and stripping, was 77.5% but it can be seen as 88%, since, although the totality of the Cu content was not stripped, it remains in the organic phase and so it can be re-extracted until an almost full efficiency is obtained. Moreover, these experiences were made in single extraction/stripping stages, and in an industrial plant a countercurrent multistage design will be applied. This way, it is believed that more than 99% of Cu could be extracted and recovered.

For the recovery of the copper contained in the strip liquor, the solution was evaporated until crystallization occurred, and the $CuSO_4$ solids obtained were filtered, washed with acetone, dried in an oven for 24 hours, calcinated at 400ºC for 6 hours, and weighed. The weighed amount of extracted $CuSO_4$ was 2.074 g.

The XRPD and EDS diffractogram revealed no sign of other contaminants.

4.5.2. Al Removal

Before starting the neutralization process, 15 mL of a 4 M NaOH solution was added to 150 mL of the Cu-free solution, the pH value increased to 4.30, and $Al(OH)_3$ started to precipitate. The Al removal resulted in 0.748 g of precipitate, expectably $Al(OH)_3$. A sample of the Al-free solution was diluted and analysed with AAS.

The extraction yield values from the AAS analysis reveal 53.6% extraction yield for Al, with considerable contamination coming from the remaining metals.

To support the results given from AAS analysis, XRPD and SEM with EDS analysis were performed in the resultant hydroxide. EDS analysis confirms the presence of Li, Ni, Mn, Co, and Cu, in the hydroxide resultant from the precipitation. XRPD reveals a non-crystalline hydroxide form, very common in products produced by neutralization, not allowing the identification of the phases present. However a small peak was found, attributed to an Al species in the form of sodium aluminium hexafluoride (Na_3AlF_6), an inorganic compound extensively used in the industrial production of aluminium metal. The F comes from the binder or the electrolyte. The Na derives from the solution used to increase the pH value. Additionally, the presence of the transition metals can be confirmed due to the fluorescence effect, caused by the transition metals.

4.5.3. Ni, Mn, and Co Precipitation

As before, the process started by adding 38 ml of the 4 M NaOH solution was added to 165 mL of the Al-free solution, in order to increase the pH value to 9.49. The precipitation resulted in 9.486 g of $NiMnCo(OH)_2$.

After precipitation, a sample was taken from the filtrate and analysed with AAS. The results present approximately 100% extraction for the transition metals. Al and Cu extraction, although showing 100% yield, induce a low contamination level since the initial concentration was extremely small, and therefore negligible.

XRPD and SEM were performed on a sample of the hydroxide so as to verify the statements made above. The EDS diffractogram corroborates the results, showing no presence of other elements besides sulphur. The XRPD diffractogram reveals an amorphous sample, with no distinguishable peaks. As in the previous sample, due to the fluorescence effect, the presence of the transition metals, Ni and Co, can be confirmed.

4.5.4. Li Precipitation

Seeing as, due to the previous separation trials, the Na content in the solution was already very high, the Li-rich solution was evaporated to half to facilitate the precipitation of Li_2CO_3 via the addition of 10 mL of a 2.5 M Na_2CO_3 solution to 94 ml of the concentrated Li-rich solution. Na_2CO_3 was chosen because with the use of the carbonate, the resulting precipitate would be Li_2CO_3, a ready-to-use compound in the LIB production [20].

The precipitated carbonate was washed with a Li_2CO_3 saturated solution, dried, and weighed, resulting in 0.558 g of Li_2CO_3.

To conclude these metal separation trials, a sample of the obtained Li_2CO_3 was analysed with SEM and XRPD. EDS revels the smallest presence of Mn in the sample but seeing as the peak is so small it can be disregarded. In addition, it also identifies big particles of sodium sulphate (Na_2SO_4)

contaminates, originated from the Na present in solution added to increase the pH value. The XRPD diffractogram confirms the formation of Li_2CO_3 and the presence of Na_2SO_4 and reveals no presence of Mn. To tackle this contamination issue, the precipitate should be washed with a saturated Li_2CO_3 solution.

5. Conclusions

This work aimed at the development of a hydrometallurgical recycling process that could potentially be adapted to an industrial scale.

Thermal treatment and solvent dissolution were performed in samples of the electrode materials and only calcination unveiled disaggregation of 100%. For the anodes, disaggregation was generally inefficient. The electrode cells were further studied, and the conclusion reached was that the cathode powder represented 90 and 80% of the electrode weight for cells 5 and 7, respectively, the balance being the Al conductive foils.

The impact of calcination in the leaching behaviour of the cathode metals (Li, Ni, Co, Mn) was also investigated revealing that the thermal treatment at 400ºC for 5 hours was the optimal condition due to the obtained leaching yields. Additionally, the impact of the reducer, introducing the possibility of electrode foils as reducers, was also considered and revealed that using $Na_2S_2O_5$, or a combination of $Na_2S_2O_5$ with the electrode foils, were the leading alternatives. Nonetheless, the addition of electrode foils did not justify the increase of contaminants in the leaching liquor.

Previous to the final set of leaching experiments, two batches of mixed electrode material, one calcinated and another non-treated, underwent crushing and sieving. After careful consideration of all results, the conclusion reached was that the calcinated crushed material presented better signs of disaggregation. 0.5 mm was chosen as the parting sieve, i.e. the sieve that better separates the powder fractions from the foil fractions.

The leaching of the electrode metal was efficiently achieved, with optimal leaching conditions of 3 M of H_2SO_4 as leaching agent, 0.25 M of $Na_2S_2O_5$ as reducing agent, an L/S ratio of 5 L/kg, temperature of 80ºC, for 30 minutes, presenting leaching yields for Li, Ni, Mn, Co, Cu, and Al of approximately 95%, 100%, 100%, 98%, 100%, and 73%, respectively. Under the optimized conditions, the leach residue was composed of graphite with good purity.

To end, an introduction to the metal separation processes was developed. $CuSO_4$ was separated and produced after solvent extraction with 20 v% ACORGA M5640 diluted in ESCAID 102. Purification by neutralization to pH 4.30 allowed the removal of most part of the aluminium, contaminated with some Li, Ni, Mn, Co, and Cu. A mixed hydroxide $NiMnCo(OH)_2$ was precipitated via the addition of NaOH to pH 9.49, where about an average 99.98% of recovery of the three metals was achieved. Finally, Li_2CO_3 was obtained by precipitation with the addition of Na_2CO_3, contaminated with Na_2SO_4, requiring further investigation to optimize precipitation conditions, and washing procedures.

In conclusion, the process presented satisfactory yields in each step and could easily be scaled up to an industrial scale.

References

[1]   European Commission, Strategic Research Agenda for Batteries 2020, *European Commission*, **2020**,.

[2]   Xu, L.;Yilmaz, H.Ü.;Wang, Z.;Poganietz, W.R.;Jochem, P., Greenhouse Gas Emissions of Electric Vehicles in Europe Considering Different Charging Strategies, *Transportation Research Part D 87*, **2020**, *87*, 102534. doi:*10.1016/j.trd.2020.102534*.

[3]   Bonsu, N.O., Towards a Circular and Low-Carbon Economy: Insights from the Transitioning to Electric Vehicles and Net Zero Economy, *Journal of Cleaner Production*, **2020**, *256*, 120659. doi:*10.1016/j.jclepro.2020.120659*.

[4]   Wang, M.;Tian, Y.;Liu, W.;Zhang, R.;Chen, L.;Luo, Y.;Li, X., A Moving Urban Mine: The Spent Batteries of Electric Passenger Vehicles, *Journal of Cleaner Production*, **2020**, *265*, 121769. doi:*10.1016/j.jclepro.2020.121769*.

[5]   Arshad, F.;Li, L.;Amin, K.;Fan, E.;Manurkar, N.;Ahmad, A.;Yang, J.;Wu, F.;Chen, R., A Comprehensive Review of the Advancement in Recycling the Anode and Electrolyte from Spent Lithium Ion Batteries, *ACS Sustainable Chemistry*

and Engineering, **2020**, *8*, 13527–13554. doi:*10.1021/acssuschemeng.0c04940*.

[6] Sommerville, R.;Zhu, P.;Rajaeifar, M.A.;Heidrich, O.;Goodship, V.;Kendrick, E., A Qualitative Assessment of Lithium Ion Battery Recycling Processes, *Resources, Conservation and Recycling*, **2021**, *165*, 105219. doi:*10.1016/j.resconrec.2020.105219*.

[7] Mossali, E.;Picone, N.;Gentilini, L.;Rodrìguez, O.;Pérez, J.M.;Colledani, M., Lithium-Ion Batteries towards Circular Economy: A Literature Review of Opportunities and Issues of Recycling Treatments, *Journal of Environmental Management*, **2020**, *264,* 110500. doi:*10.1016/j.jenvman.2020.110500*.

[8] Asadi Dalini, E.;Karimi, G.;Zandevakili, S.;Goodarzi, M., A Review on Environmental, Economic and Hydrometallurgical Processes of Recycling Spent Lithium-Ion Batteries, *Mineral Processing and Extractive Metallurgy Review*, **2020**, *42,* 451–472. doi:*10.1080/08827508.2020.1781628*.

[9] Yan, S.;Sun, C.;Zhou, T.;Gao, R.;Xie, H., Ultrasonic-Assisted Leaching of Valuable Metals from Spent Lithium-Ion Batteries Using Organic Additives, *Separation and Purification Technology*, **2021**, *257,* 117930. doi:*10.1016/j.seppur.2020.117930*.

[10] Chen, X.;Li, J.;Kang, D.;Zhou, T.;Ma, H., A Novel Closed-Loop Process for the Simultaneous Recovery of Valuable Metals and Iron from a Mixed Type of Spent Lithium-Ion Batteries, *Green Chemistry*, **2019**, *21,* 6342–6352. doi:*10.1039/c9gc02844g*.

[11] Yang, Y.;Okonkwo, E.G.;Huang, G.;Xu, S.;Sun, W.;He, Y., On the Sustainability of Lithium Ion Battery Industry – A Review and Perspective, *Energy Storage Materials*, **2021**, *36*, 186–212. doi:*10.1016/j.ensm.2020.12.019*.

[12] Armand, M.;Axmann, P.;Bresser, D.;Copley, M.;Edström, K.;Ekberg, C.;Guyomard, D.;Lestriez, B.;Novák, P.;Petranikova, M.;Porcher, W.;Trabesinger, S.;Wohlfahrt-Mehrens, M.;Zhang, H., Lithium-Ion Batteries – Current State of the Art and Anticipated Developments, *Journal of Power Sources*, **2020**, *479,* 228708. doi:*10.1016/j.jpowsour.2020.228708*.

[13] Chen, X.;Li, J.;Kang, D.;Zhou, T.;Ma, H., Novel Closed-Loop Process for the Simultaneous Recovery of Valuable Metals and Iron from a Mixed Type of Spent Lithium-Ion Batteries, *Green Chemistry*, **2019**, *21,* 6342–6352. doi:*10.1039/c9gc02844g*.

[14] Xiao, J.;Li, J.;Xu, Z., Challenges to Future Development of Spent Lithium Ion Batteries Recovery from Environmental and Technological Perspectives, *Environmental Science and Technology*, **2020**, *54,* 9–25. doi:*10.1021/acs.est.9b03725*.

[15] Lv, W.;Wang, Z.;Cao, H.;Sun, Y.;Zhang, Y.;Sun, Z.H.I., A Critical Review and Analysis on the Recycling of Spent Lithium-Ion Batteries, *ACS Sustainable Chemistry and Engineering*, **2018**, *6*, 1504–1521. doi:*10.1021/acssuschemeng.7b03811*.

[16] Chen, X.;Cao, L.;Kang, D.;Li, J.;Li, S.;Wu, X., Hydrometallurgical processes for valuable metals recycling from spent lithium-ion batteries, *Springer*, **2019**, ISBN:9783030318345doi:*10.1007/978-3-030-31834-5*.

[17] Chen, X.;Cao, L.;Kang, D.;Li, J.;Li, S.;Wu, X., Hydrometallurgical processes for valuable metals recycling from spent lithium-ion batteries, **2019**, ISBN:9783030318345doi:*10.1007/978-3-030-31834-5*.

[18] He, L.-P.;Sun, S.-Y.;Song, X.-F.;Yu, J.-G., Recovery of Cathode Materials and Al from Spent Lithium-Ion Batteries by Ultrasonic Cleaning, *Waste Management*, **2015**, *46,* 523–528. doi:*10.1016/j.wasman.2015.08.035*.

[19] Castrejón-Sánchez, V.H.;Solis, A.C.;López, R.;Encarnación-Gomez, C.;Morales, F.M.;Vargas, O.S.;Mastache-Mastache, J.E.;Sánchez, G.V., Thermal Oxidation of Copper over a Broad Temperature Range: Towards the Formation of Cupric Oxide (CuO), *Materials Research Express*, **2019**, *6,*doi:*10.1088/2053-1591/ab1662*.

[20] Ma, Y.;Svärd, M.;Xiao, X.;Gardner, J.M.;Olsson, R.T.;Forsberg, K., Precipitation and Crystallization Used in the Production of Metal Salts for Li-Ion Battery Materials: A Review, *Metals*, **2020**, *10*, 1–16. doi:*10.3390/met10121609*.