# Metals recovery from end-of-life Li-ion batteries by physical processing and hydrometallurgical treatment

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## Introduction

The growing demand for lithium-ion batteries (LIB) for electric mobility and energy storage applications has created enormous pressure on the metals market, not only for lithium (Li) but also for other critical metals such as nickel (Ni), cobalt (Co) and manganese (Mn). Beyond the need for primary extraction of mineral resources, which is essential for an initial phase of significant growth in demand, recycling will quickly play a fundamental role in the availability of these raw materials. Recycling also allows a valuable contribution to the management of end-of-life batteries (Dobó *et al.*, 2023). Recycling of LIB is predominantly conducted through hydrometallurgical methods, involving both physical/mechanical processes (such as electrode fraction concentration) and chemical processes (including leaching, separation and recovery).

The physical operations include safe discharge and dismantling, followed by shredding and separation of fractions (Sommerville *et al.*, 2020). In hydrometallurgical processing, metals are leached and recovered from aqueous solutions using different methods (Bae and Kim, 2021). This work presents findings from research on the physical and chemical treatment of end-of-life LIB (Ni-Co-Mn or NCM type), with an emphasis on the obtained recoveries and yields.

## Materials and Methods

In the physical processing experiments, LIB-NCM pouch cells were ground in a laboratorial shredder and were sieved for particle size characterization. Samples were collected for chemical analysis to evaluate metal contents and recoveries. In this work, hydrometallurgical tests were carried out in stirred laboratory reactors, under controlled conditions, including black mass leaching, followed by contaminants removal and metal recovery operations. Chemical analysis of solutions and solids were conducted by atomic absorption spectrometry (Perkin-Elmer PinAAcle 500®) to assess metal yields.

## Results and Discussion

In the physical processing studies, the main objective was to evaluate the recovery of the black mass (mixture of anode and cathode powders) in the fine fractions of the shredded material. The analysis of the fractions revealed that the separation and recovery of the black mass was better achieved when the discharge grid aperture of the shredder was smaller. After applying a sieving operation after the shredding, it was possible to assess the optimal separation sieve to be applied to recover part of the electrode fine fractions with minimum contamination with aluminium (Al) and copper (Cu) (Figure 1). Optimal NCM cathode recovery and selectivity were achieved with a 4 mm grid, due to longer residence time that aided efficient particle liberation. With this grid and using a 1 mm sieve size in the subsequent sieving operation, it yielded over 60% NCM recovery and low Al/Cu contamination.

Hydrometallurgical processing follows physical separation and entails the leaching of the black mass concentrate, followed by additional separation and recovery steps such as precipitation, solvent extraction and crystallization. Leaching, as the first step of hydrometallurgy, can be performed by different reagents, namely acids and other additives, aiming at solubilizing the target metals in aqueous media. Using sulfuric acid solutions, the cathode phase $Li(Ni,Co,Mn)O_2$ reacts forming soluble sulfates, $(Ni,Co,Mn)SO_{4(aq)}$ and $Li_2SO_{4(aq)}$. Organic acid leachants, though costlier and not industrially proven, are widely regarded as more environmentally friendly alternatives (Yu *et al.*, 2024). Figure 2 presents a comparison of leaching yields obtained with sulfuric and oxalic acid leachants. The data indicates that oxalic acid demonstrates selectivity for Li, whereas sulfuric acid achieves high recovery yields across all metals. When considering sulfuric acid leaching, the following operations will involve the purification of the leaching solution (removal of co-extracted Al and Cu), followed by the separation and recovery of the cathode metals. Ni, Co and Mn can be precipitated as a mixed hydroxide, leaving soluble Li for further recovery. Alternatively, individual metal streams can be produced by applying selective separation techniques, with solvent extraction being the most adequate.

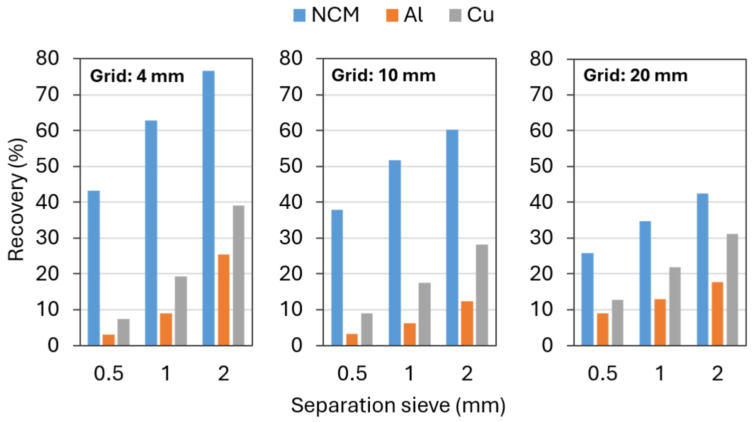

Figure 1. Recovery of cathode black mass (NCM) and contaminants (Al,Cu), as a function of separation sieving sizes, for three different shredder discharge grids.

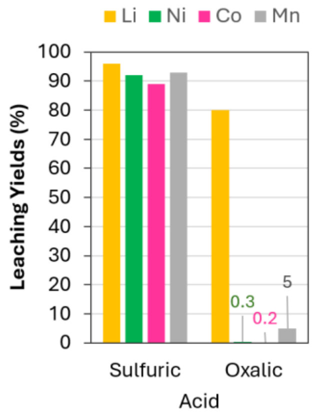

Figure 2. Metal leaching yields using sulfuric and oxalic acids (1 M, 60ºC, 1h).

## Conclusions

Physical and chemical processing stages are both crucial in the recycling of spent LIB. The physical stage enables the concentration of cathode metals within the fine fractions (of the black mass), resulting in minimal contamination with scrap materials such as Al and Cu. During the subsequent chemical stage, leaching and purification/separation processes allow the extraction of these metals for reuse in new cathodes production, thereby supporting a circular economy.

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PRR Plano de Recuperação e Resiliência
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