ADVANCED MANUFACTURING PROCESSES
FOR LOW COST GREENER LI-ION BATTERIES

HYDROMETALLURGICAL RECYCLING TREATMENT

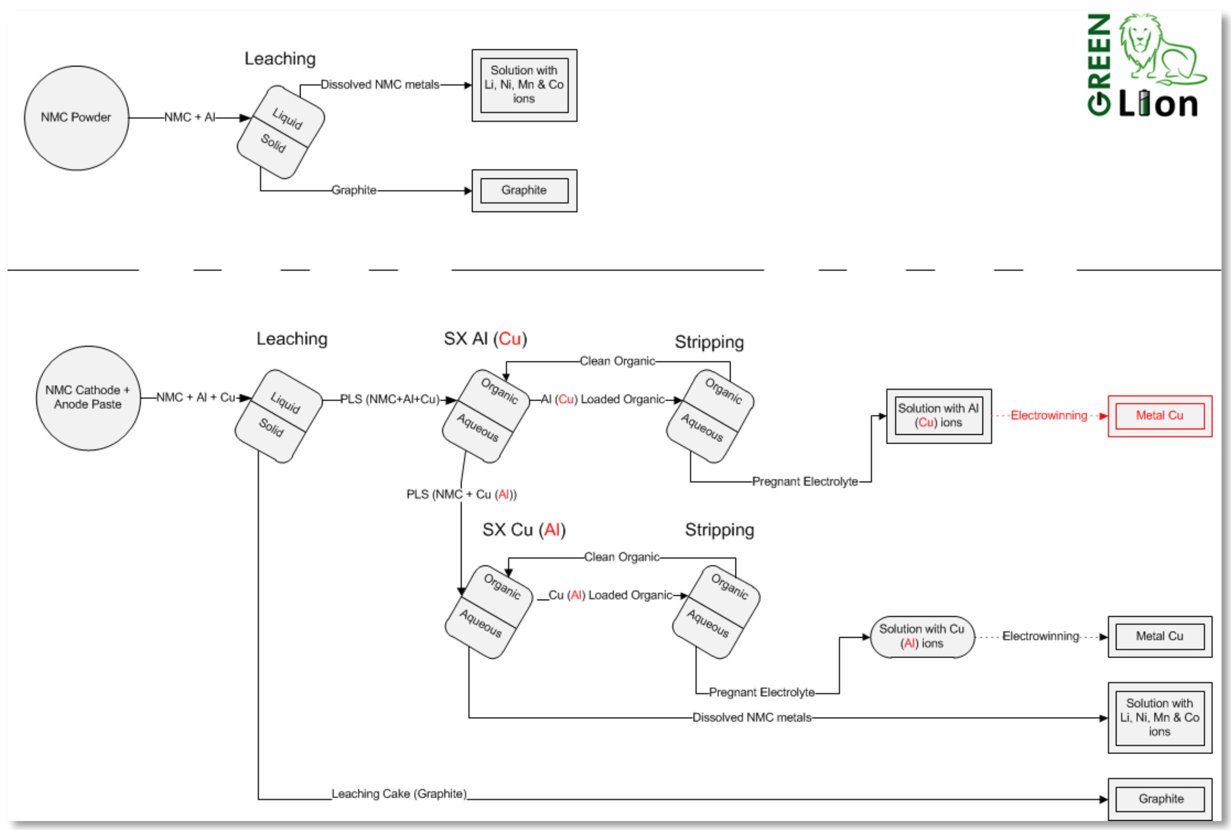
Introduction

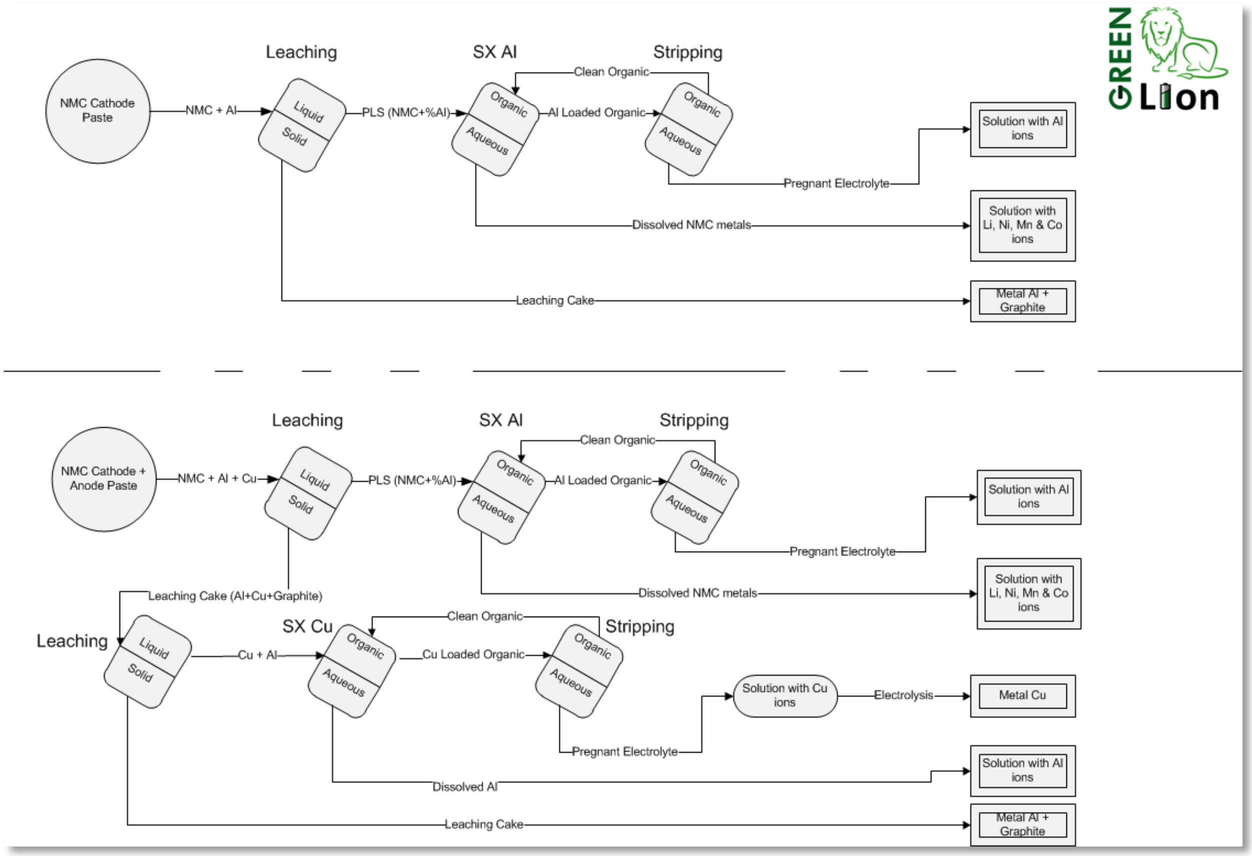
This chapter addresses the different hydrometallurgical processes that could be applied to ensure adequate valorization and complete recycling of battery cell material.

Once the pre-treatment stage of wasted, end of life, battery pouch cells is finished, the resulting dust is hydrometallurgicaly treated in order to recover battery metals (Li, Ni, Mn, Co, Cu and Al). Three different alternative pouch cell pre-treatment methods were contemplated and, accordingly, three treatment research lines were carried out, namely:

- Treatment of comminuted anode + cathode material (method 1).
- Treatment of comminuted cathode material (method 2).
- Treatment of cathode active material (method 3).

The treatment processes consist on following consecutive stages: leaching of grinded battery material in order to obtain an aqueous solution containing the battery metals, purification stage to selectively isolate elements that are further processed in the next precipitation stage in order to obtain metals or products used to make new batteries.





Metals dissolution

Leaching is the first stage of the treatment process, aiming to obtain an aqueous solution containing the battery metals from the grinded battery material.

Two different kinds of acid leachant agents have been tested for dissolving battery metals from pre-treated material:

- Industrial conventional inorganic acids (H2SO4 and HCl), which maximize metals recovery and minimize economic process costs.
- Organic acids (citric acid), as a more environmentally friendly alternative for dissolving battery metals.

All research lines have been optimized by means of DoE to fulfil such a complete study.

Industrial conventional inorganic acids

Initially, industrial inorganic acids H2SO4 and HCl, have been proved as an economically driven alternative to dissolve battery metals. The following scenarios have been assessed:

Leaching of comminuted anode + cathode material with inorganic acids ("M1I").

Leaching material consists on a mixture of active cathodic material (NMC) together with metallic aluminum and copper from the current collectors. Two different leaching strategies have been assessed as alternative processes:

- Leaching of comminuted anode + cathode material with inorganic acids: Two leaching stages ("M1I-A"). Battery metals are dissolved in the two following different leaching stages:
  - Leaching Stage 1: Cathode active materials dissolution ("M1I-A1"). It consists on a first leaching process in order to dissolve metals from cathode active material (Li, Ni, Mn and Co) and part of metallic Al, but not metallic Cu from the anode current collector. Design of Experiments results have yielded the optimal combination of process parameters that maximises NMC metals in the liquour and minimises, with minor relevance, the presence of Cu and Al, and the acid consumption:

	Metal recovery (%)						Consumptions (€/kg treat. mat.)
Acid	**Li**	**Ni**	**Mn**	**Co**	**Cu**	**Al**	**Total**
H_2SO_4	99	97	99	97	1	92	0,4

  - Leaching Stage 2: Copper and Aluminium dissolution ("M1I-A2"). This second leaching stage is designed to totally recover metallic Cu and Al from the solid residue of leaching stage 1. Optimal results prioritizing the maximisation of Cu leaching efficiency, and also considering the acid consumption as a secondary important response, yield a recovery of:

	Metal recovery (%)		Consumptions (€/kg treat. mat.)
Acid	**Cu**	**Al**	**Total**
HCl	99	61	1,2

- Leaching of comminuted anode + cathode material with inorganic acids: One total leaching stage ("M1I-B."). Cathode active material metals and metallic Cu and Al are dissolved together in one unique leaching stage. Results of design of experiments have been assessed to maximize all metals dissolution and minimize acid and oxidant consumptions, yielding following optimal results:

	Metal recovery (%)						Consumptions (€/kg treat. mat.)
Acid	**Li**	**Ni**	**Mn**	**Co**	**Cu**	**Al**	**Total**
H_2SO_4	>99	>99	>99	>99	>99	96	3,8
HCl	>99	>99	>99	>99	>99	>99	1,5

Leaching of comminuted cathode material with inorganic acids (“M2I”):

Leaching material consists on the active cathodic material (NMC) and the metallic aluminum from the current collector. After interpretation of DoE results and an additional kinetic study, optimal results for maximization of metals leaching and minimization, with a minor relevance, of acid consumption are:

	Metal recovery (%)						Consumptions (€/kg treat. mat.)
Acid	**Li**	**Ni**	**Mn**	**Co**	**Cu**	**Al**	**Total**
H_2SO_4	>99	>99	>99	>99	-	97	0,8

Leaching of cathode active material with inorganic acids (“M3I”):

In this case, leaching material only contains the active cathodic material (NMC) and a small quantity of graphite. Laboratory leaching tests and DoE results have yielded these optimal results, aiming to maximize metals dissolution and minimize reagents and energetic costs:

	Metal recovery (%)						Consumptions (€/kg treat. mat.)
Acid	**Li**	**Ni**	**Mn**	**Co**	**Cu**	**Al**	**Total**
H_2SO_4	97	96	97	97	-	97	2,1

Organic acids

Citric acid has been assessed as a more environmentally friendly alternative for dissolving battery metals.

Citric acid has been evaluated as leachant agent for the cases of comminuted anode and cathode material (M1O) and just only cathode active material (M3O) to be leached:

Leaching of comminuted anode + cathode material with citric acid (“M1O”).

A design of experiments was carried out aiming to maximising NMC metals leaching and minimize reagents consumptions, yielding these optimal results:

	Metal recovery (%)						Consumptions (€/kg treat. mat.)
Acid	**Li**	**Ni**	**Mn**	**Co**	**Cu**	**Al**	**Total**
Citric	99	99	>99	>99	13	12	41,6

Leaching of cathode active material with citric acid (“M3O”):

Optimal results for maximization of metals dissolution and minimization with minor relevance of reagents and energetic consumption, are the following:

		Metal recovery (%)						Consumptions (€/kg treat. mat.)
	Acid	**Li**	**Ni**	**Mn**	**Co**	**Cu**	**Al**	**Total**
	Citric	97	96	96	96	-	96	4,6

Metals Purification

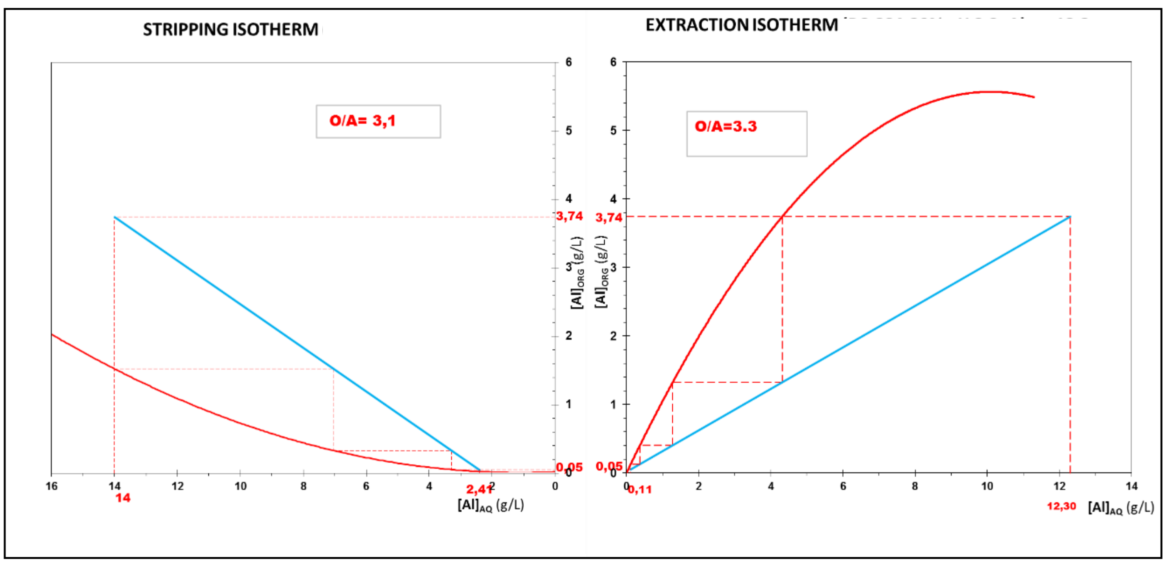
The purification stage aims to selectively isolate elements that can be further processed in the precipitation stage for metal recovery and/or used as the starting point for the production of commercial products.

Purification stage basically consists on treating the aqueous solution and the solid residue obtained in the leaching stage in order to obtain: a purified solution just containing the cathode active material metals; purified copper for the synthesis of reusable copper products; and purified aluminum for the synthesis of reusable aluminum products.

Solvent extraction technique has been assessed for this separation purpose proving successfully the separation of Al and Cu from the solution containing the cathode active material metals:

Aluminum Solvent extraction

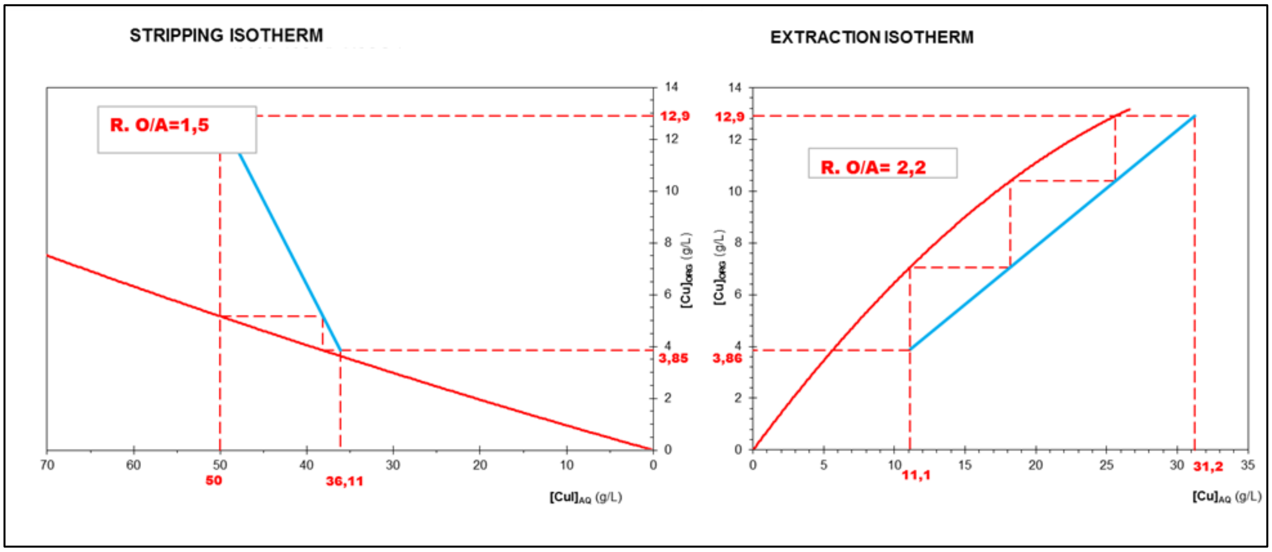
Solvent extraction has been assessed as a technique for separation of dissolved Al from NMC metals.
It has been proved that Al can be removed from the pregnant leaching solution by means of solvent extraction, generating an aqueous raffinate containing the cathode active metals (Li, Ni, Mn and Co), an organic reextracted phase which is recycled again to SX system and an Al purified aqueous liquor, which can be used for the synthesis of reusable aluminum products.



Copper Solvent extraction

Copper Solvent extraction (SX) has been tested as an alternative technique to separate Cu from Al and NMC metals.

A Cu purified aqueous liquor is obtained from the pregnant leaching solution by means of solvent extraction. This purified Cu liquor can be reused for the synthesis of different Copper products. The reextracted organic phase and the aqueous Cu raffinate are recycled again to SX system to reuse the organic extractant and minimize Cu losses.

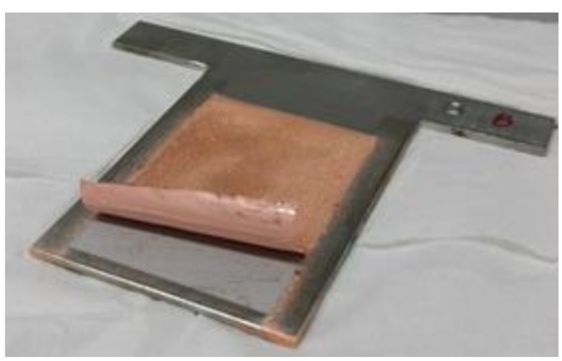


Metals precipitation for further uses

The precipitation stage aims to transform purified intermediate from purification stage into reusable products for the synthesis of new batteries or another uses.

The final products of the precipitation stage consist of:

- Liquid products:
  - A purified solution just containing the cathode active material metals (Li, Ni, Mn, Co and also a small amount of Al), which is planned to be used by cathode manufactures (Solvay) for the production of new recycled cathode active material.
  - High purity $Al_2(SO_4)_3$ obtained from solvent extraction of Al, which can be directly commercialised for many different industrial applications (sewage treatment, clarification of potable water, industries of pulp and paper/ fats and soap/oil/pharmaceutical...)
- Solid products:
  - High purity metallic Cu, obtained by electrowinning of purified $CuSO_4$ from solvent extraction of Cu, which can be used for the synthesis of new anodes current collectors or other reusable copper products.



- Aluminium/Copper rich sub-products, coming out of the leaching stage, which can be integrated back into the effluent feed of the leaching stages in order to maximise the recovery of Cu and Al.