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Laboratório Nacional de Energia e Geologia, I. P.

Leaching as the first step of hydrometallurgy in the recycling of metals from end-of-life products

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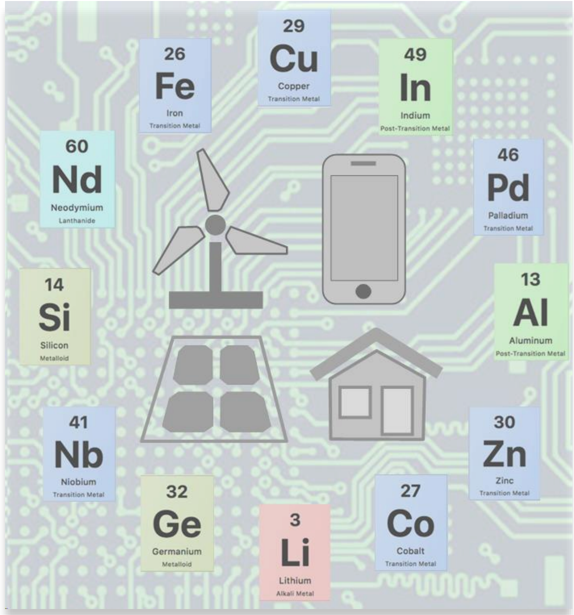
OUTLINE

- Short overview of hydrometallurgy and leaching in metals recycling
- Leaching requirements
- Case study 1 – Ammoniacal leaching of spent Zn-Mn batteries
- Case study 2 – Chloride-oxidizing leaching of PGMs from spent auto-catalysts
- Case study 3 – Reductive leaching of electrode powders of end-of-life Li-ion batteries
- Final remarks – Hydrometallurgy in Portugal

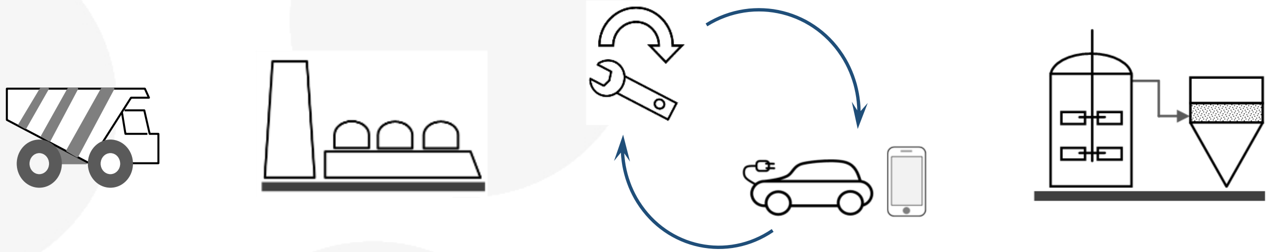
Short Overview

- The availability of Raw Materials in being discussed worldwide as one of the most important bottlenecks of technological advancements in crucial sectors:

  Energy, Environment, Health, Electronics/Computing, Defence, ...



- Efficient Management of Raw Materials involves:
  - Sustainable Extraction from **Mineral Resources**
  - Increasing **Lifetime** of products (Circular Economy)
  - Reuse, promoting **Second-life** options;
  - **Recycling** end-of-life products



Short Overview

Recycling options for metal-bearing wastes and EOL products

EOP / Wastes

Pre-treatments

Dismantling

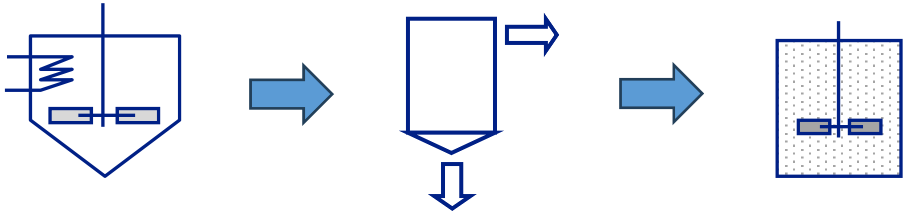
Shredding
Drying/Evaporation
Thermal treatment
Physical Processing

DIRECT RECYCLING

HYDROMETALLURGY

PIROMETALLURGY

Less energy-intensive
Less gaseous emissions
Higher versatility
Higher metal recoveries



LEACHING

Purification
Separation

Recovery

Leaching requirements

Leaching is the first step of hydrometallurgical processing, and shall provide:

- Formation of metal species, soluble in the aqueous media
- High dissolution yields
- Selectivity against impurities
- Adequate integration with the following separation / recovery operations

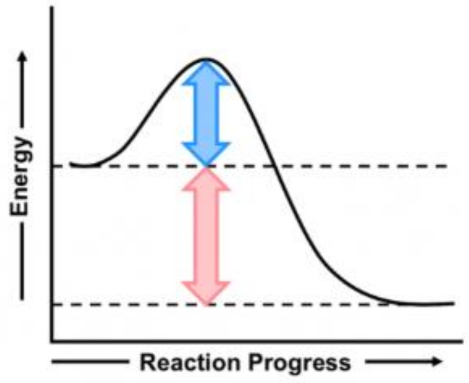
With, simultaneously:

- Low reagents and energy consumption / low costs
- Recyclability of excess chemical reagents

Key-factors in Leaching Design

Thermodynamics

- Reaction occurs spontaneously
- Products are stable



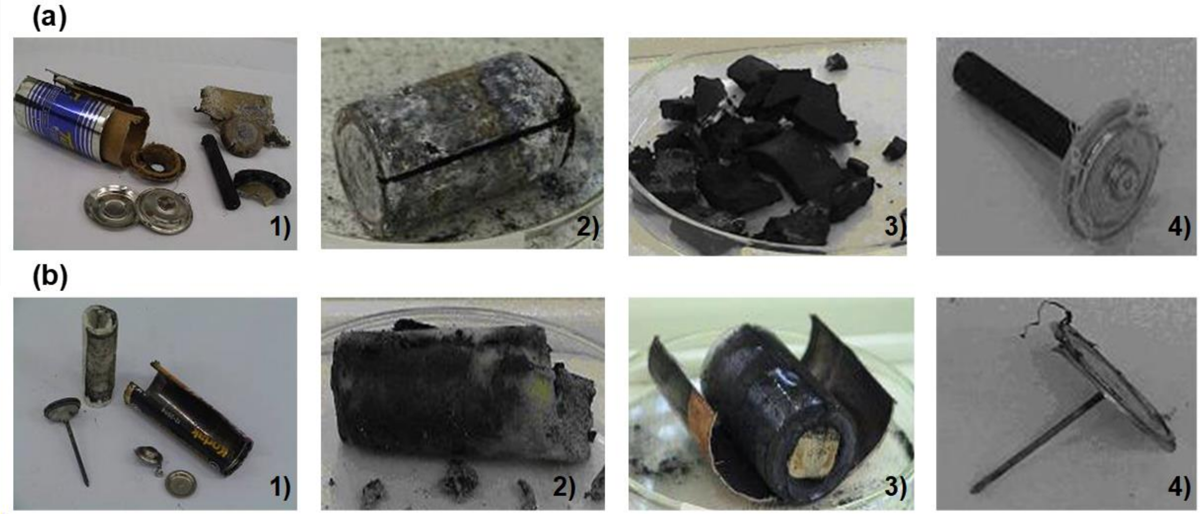
Kinetics

- Reaction time
- Reaction mechanism and rate laws
- Reactors design

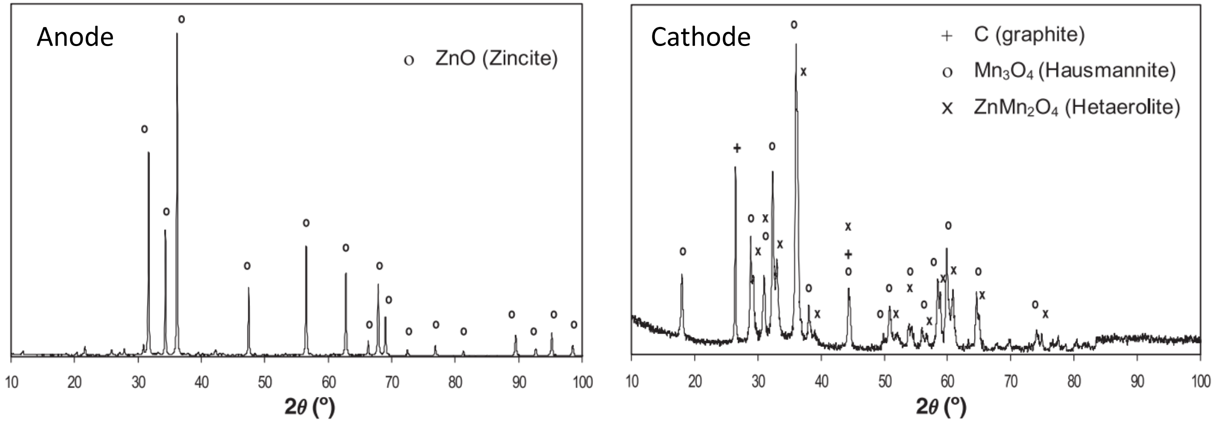
Case study 1 | Ammoniacal leaching of spent Zn-Mn batteries

The use of ammoniacal leaching can provide selectivity of zinc leaching over manganese and iron (the main contaminant)

Saline and Alkaline Zn-MnO_2 spent batteries



XRD patterns

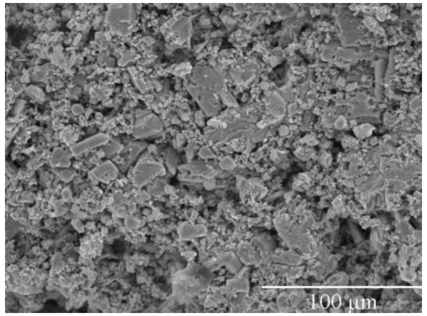


Main metal phases present:

Zinc oxide – ZnO (zincite)
Zn-Mn oxide – $ZnMn_2O_4$ (hetaerolite)
Manganese (II/III) oxide – Mn_3O_4 (haumannite)
Manganese (IV) oxide – MnO_2 (ramsdellite), *traces*

Elemental composition of black-mass
(shredded cells, no physical separation)

Metal	Zn	Mn	Fe
wt%	20	25	23

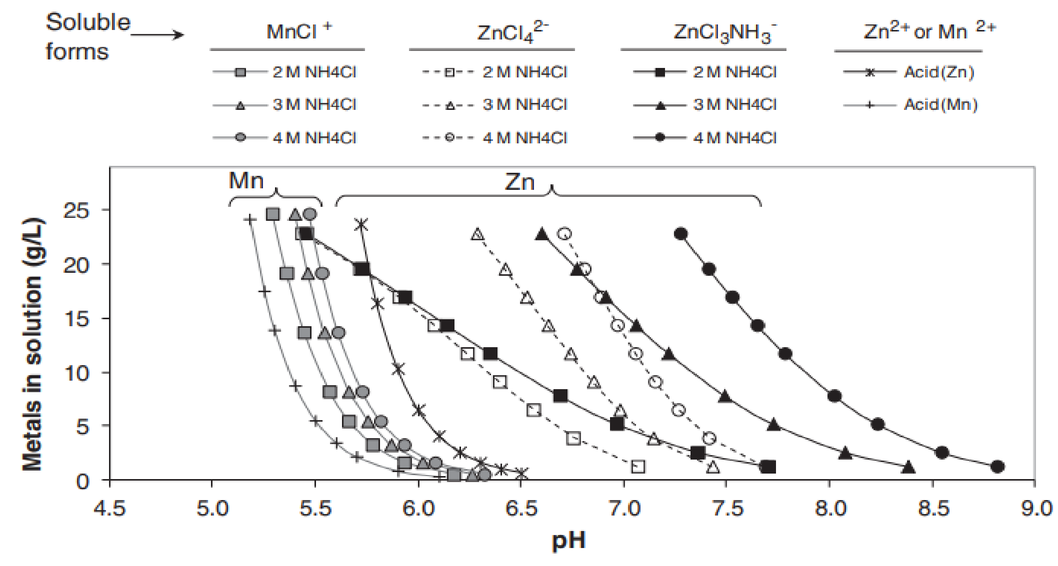


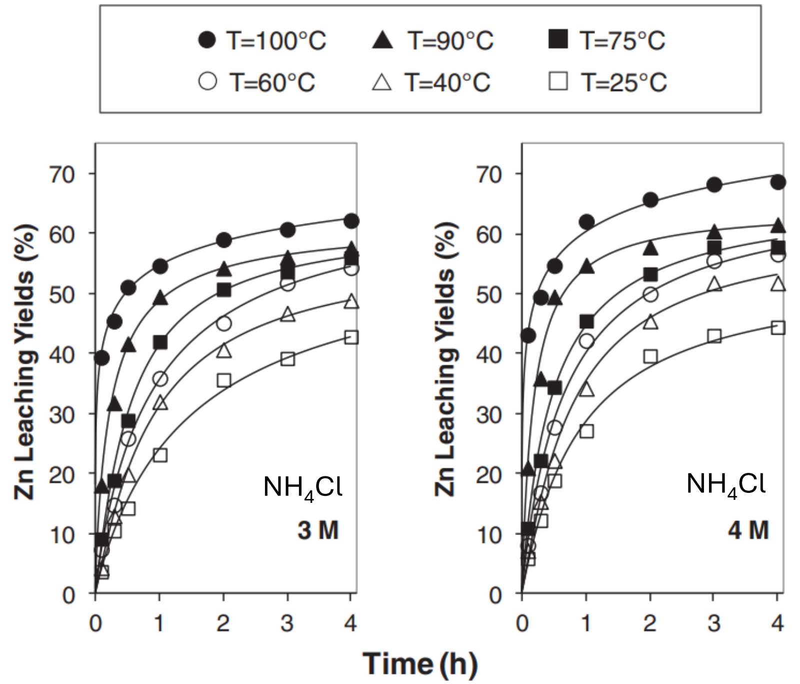
Case study 1 | Ammoniacal leaching of spent Zn-Mn batteries

The use of ammoniacal leaching can provide selectivity of zinc leaching over manganese and iron (the main contaminant)

Leaching of Zn-MnO_2 spent battery fractions with NH_4Cl

Zn ammine / chloride complexes are more thermodynamically stable than Mn





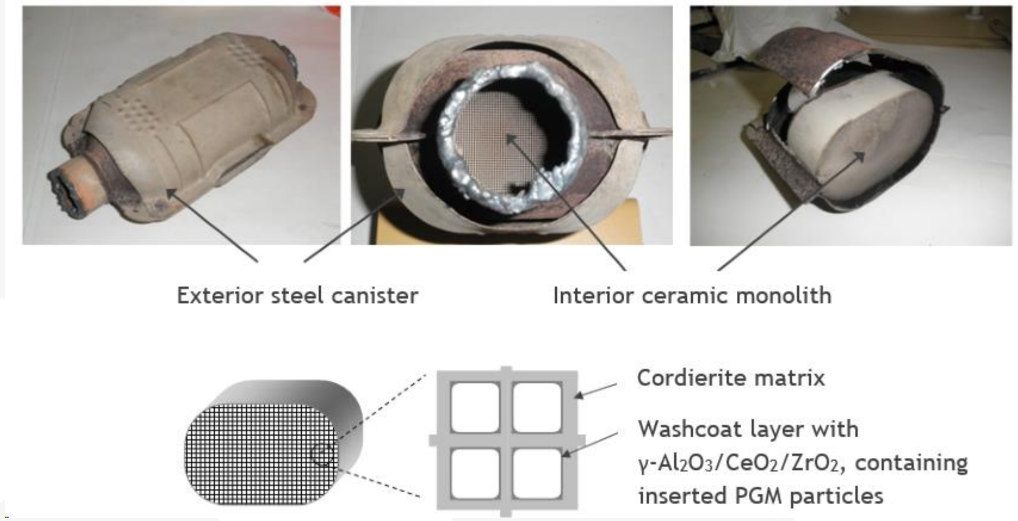
- ZnO was solubilized in ammoniacal media.
- Zn-Mn mixed oxides, as well as Mn oxides were almost not solubilized
- Fe was also not leached

Metal	Zn	Mn	Fe
Leachate composition (g/L)	6.1-6.7	0.06-0.10	<0.005
Leaching yields (%)	61-67%	< 1%	<0.04%

Case study 2 | Chloride-oxidizing leaching of PGMs from spent auto-catalysts

Platinum-group metals are noble metals, requiring highly oxidizing and complexing media to be soluble

Autocatalytic converters



Examples of elemental chemical composition of commercial catalytic converters
(grinded monoliths after dismantling)

Type	PGM (mg/kg)			Matrix (wt%)			Others
	Pt	Pd	Rh	Al	Ce	Mg	
Pd-Rh	-	397-475	97-175				
Pt-Rh	1500	-	120	15-25	3-5	6-6.5	Ca, Fe, Cr, Zn, Ni
Pt-Pd-Rh	1020	3500	200				

PGMs Leaching requires:

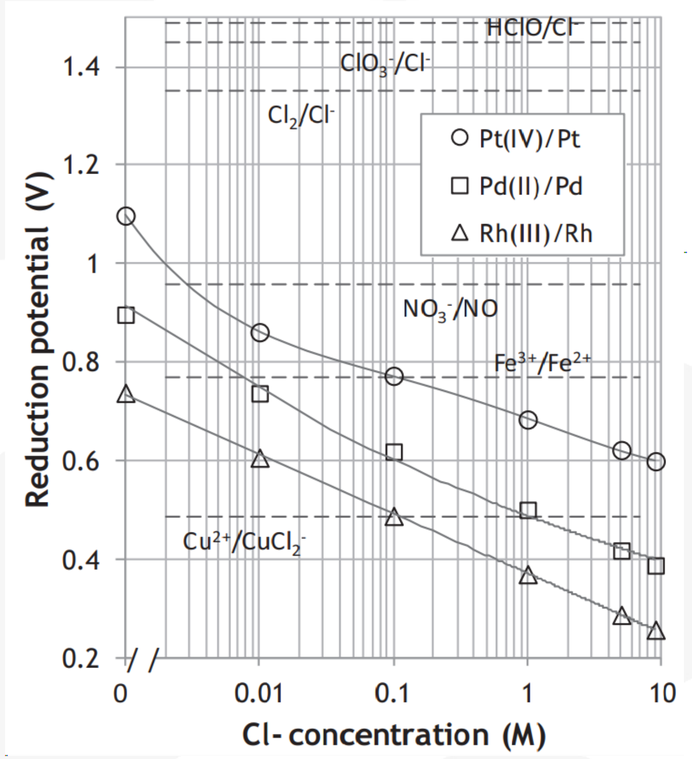
- **Complexing media, usually highly concentrated chloride media (HCl) to allow stability of aqueous chlorocomplexes;**
- **Oxidizing media, to transform metallic species to ions, using Cl_2, HNO_3, H_2O_2, NaClO, $NaClO_4$, …**

The leaching media is normally “aggressive” and environmentally “unfriendly”.

Case study 2 | Chloride-oxidizing leaching of PGMs from spent auto-catalysts

Platinum-group metals are noble metals, requiring highly oxidizing and complexing media to be soluble

Our Proposal: Use more friendly oxidizers: **Cu^{2+}**



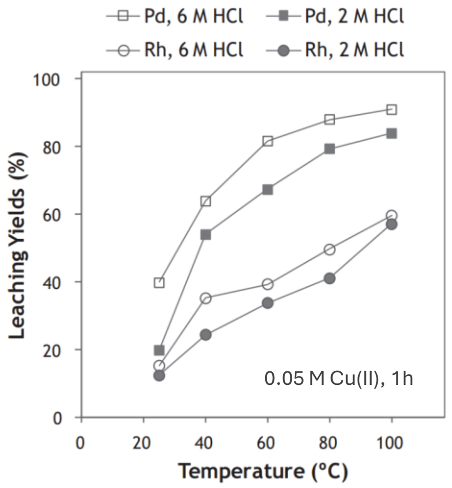
$$Pt_{(s)} + 4Cu^{2+}{}_{(aq)} + 14Cl^{-}{}_{(aq)} = PtCl_6{}^{2-}{}_{(aq)} + 4CuCl_2{}^{-}{}_{(aq)}$$

$$Pd_{(s)} + 2Cu^{2+}{}_{(aq)} + 8Cl^{-}{}_{(aq)} = PdCl_4{}^{2-}{}_{(aq)} + 2CuCl_2{}^{-}{}_{(aq)}$$

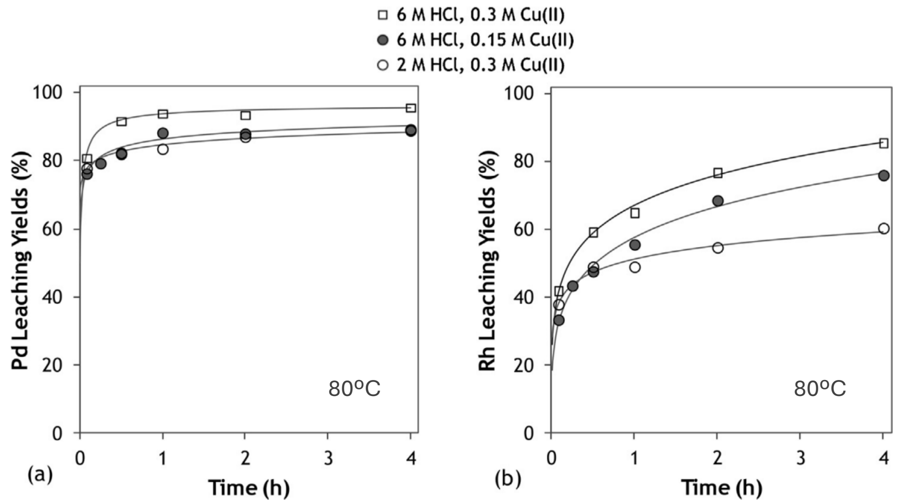
$$Rh_{(s)} + 3Cu^{2+}{}_{(aq)} + 12Cl^{-}{}_{(aq)} = RhCl_6{}^{3-}{}_{(aq)} + 3CuCl_2{}^{-}{}_{(aq)}$$

Features:

- Chloride medium **reduces the normal redox potentials**, facilitating oxidation and subsequent dissolution;
- The pair **Cu(II)/Cu(I)** coexists in chloride media, but not in sulphate or nitrate media.
- Cu^{2+} can thermodynamically **oxidize Pd, partially Rh and fairly Pt**



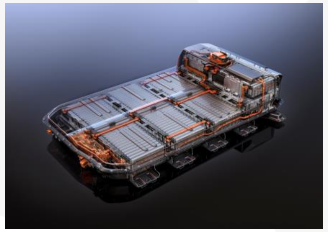
Leaching of Pd-Rh catalyst



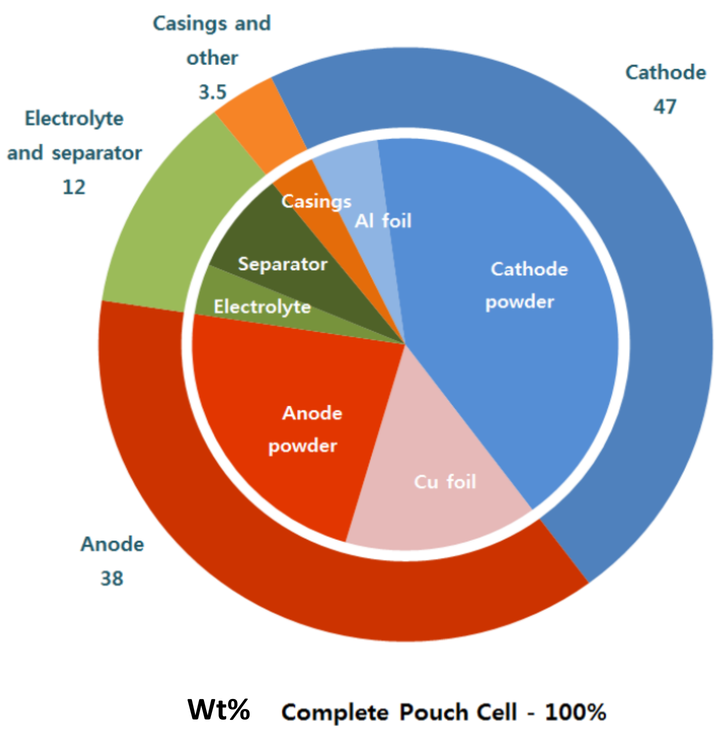
Case study 3 | Reductive leaching of electrode powders of end-of-life Li-ion batteries

NCM-type cathodes of Li-ion batteries require reduction of Mn/Co/Ni to state 2+ to be soluble

Battery packs, modules and cells



Main components



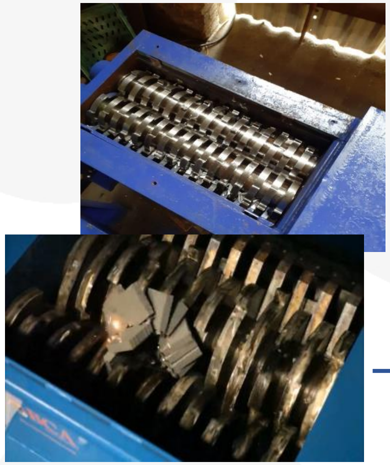
Elemental composition

Element	Composition (wt%)									
	In battery pack					In battery cell				
	LCO	NCM	NCA	LMO	LFP	LCO	NCM	NCA	LMO	LFP
Lithium	1.01	1.12	1.15	0.93	0.71	1.80	2.00	2.04	1.64	1.26
Nickel	-	3.24	7.46	-	-	-	5.75	13.3	-	-
Cobalt	8.58	3.24	1.40	-	-	15.2	5.75	2.49	-	-
Manganese	-	2.98	-	7.22	-	-	5.29	-	12.8	-
Aluminium	-	-	0.20	-	-	-	-	0.36	-	-
Iron	-	-	-	-	5.84	-	-	-	-	10.4
Phosphorus	-	-	-	-	3.16	-	-	-	-	5.62
Oxygen	4.67	5.21	5.07	5.95	6.54	8.28	9.24	9.00	10.6	11.6

Case study 3 | Reductive leaching of electrode powders of end-of-life Li-ion batteries

NCM-type cathodes of Li-ion batteries require reduction of Mn/Co/Ni to state 2+ to be soluble

LIBs Treatment

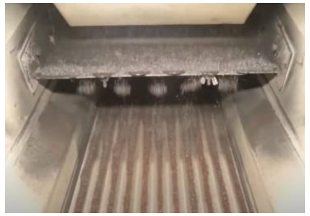


Shearing / Shredding

Organic electrolyte Evaporation / Distillation

Sieving – impure "black-mass"

Physical separation



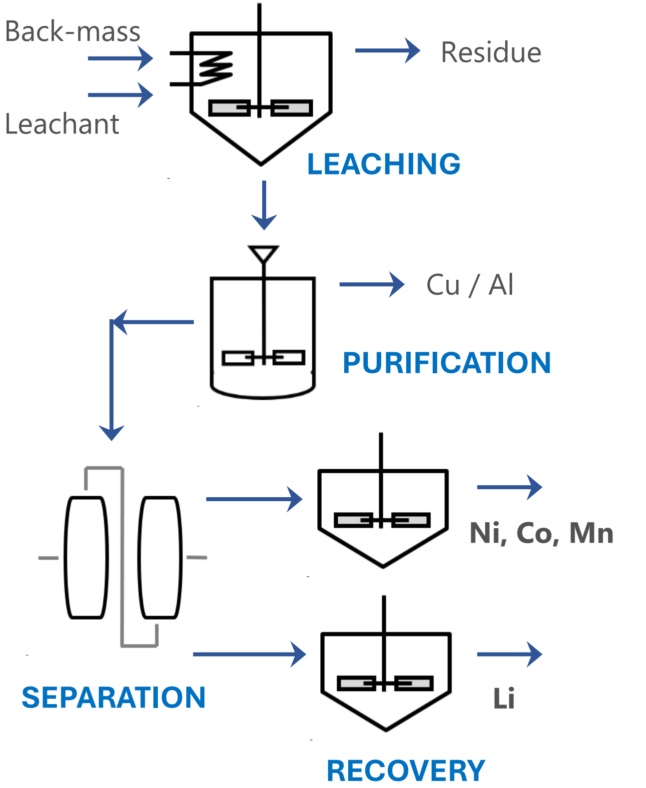
Copper

Aluminium

Black-mass – electrodes concentrate, with Cu and Al impurities

to HIDROMETAURGY

Hydrometallurgical Processing

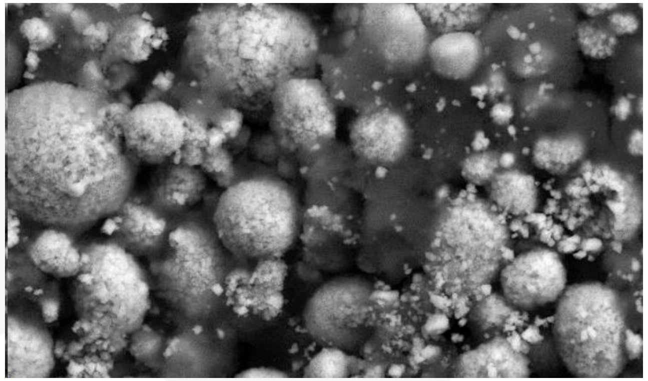


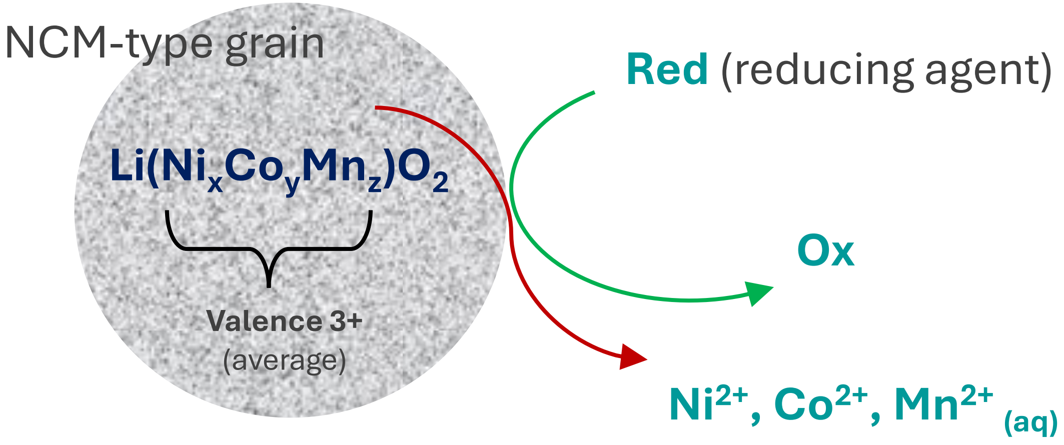
Images: BHS-Sonthofen

https://www.bhs-sonthofen.com/en/batteries
https://www.youtube.com/watch?v=IkSrLI-J9L4

Case study 3 | Reductive leaching of electrode powders of end-of-life Li-ion batteries

NCM-type cathodes of Li-ion batteries require reduction of Mn/Co/Ni to state 2+ to be soluble





Among the various possible reducers, two can be highlighted:

- **Hydrogen peroxide (H_2O_2), a reducer** for the **trivalent metals M=Ni,Mn,Co oxides** but eventually **an oxidizer** for other species like **copper**

$$2\,LiMO_{2\,(s)} + H_2O_{2\,(aq)} + 3\,H_2SO_{4\,(aq)} = Li_2SO_{4\,(aq)} + 2\,MSO_{4\,(aq)} + O_{2\,(g)} + 4\,H_2O_{(l)}$$

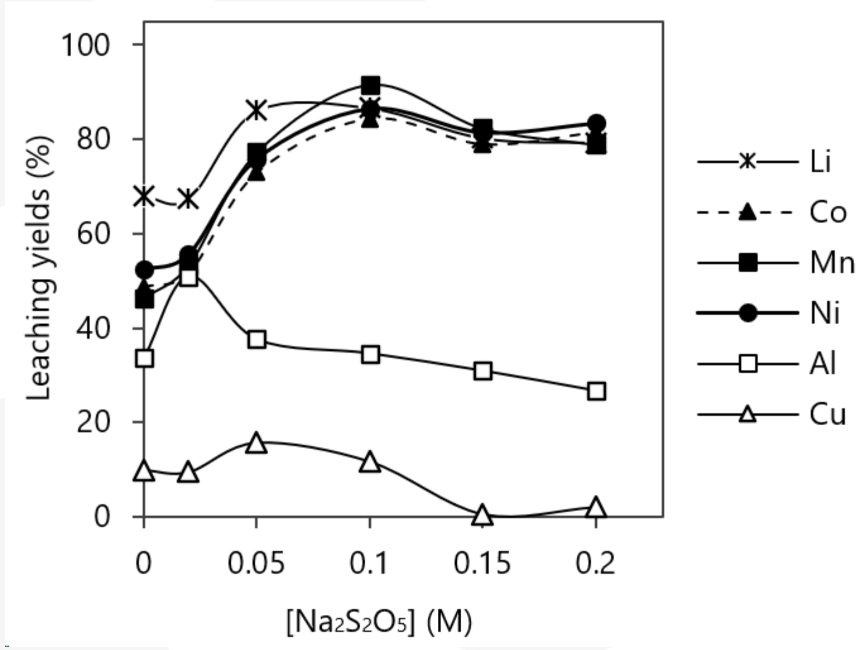
- **Sodium metabisulphite ($Na_2S_2O_5$), a reducer** for the **trivalent metals M= Ni,Mn,Co oxides**, and also for other species

$$4\,LiMO_{2\,(s)} + Na_2S_2O_{5\,(aq)} + 6\,H_2SO_{4\,(aq)} = 2\,Li_2SO_{4\,(aq)} + 4\,MSO_{4\,(aq)} + 2\,NaHSO_{4\,(aq)} + 5\,H_2O_{(l)}$$

Case study 3 | Reductive leaching of electrode powders of end-of-life Li-ion batteries

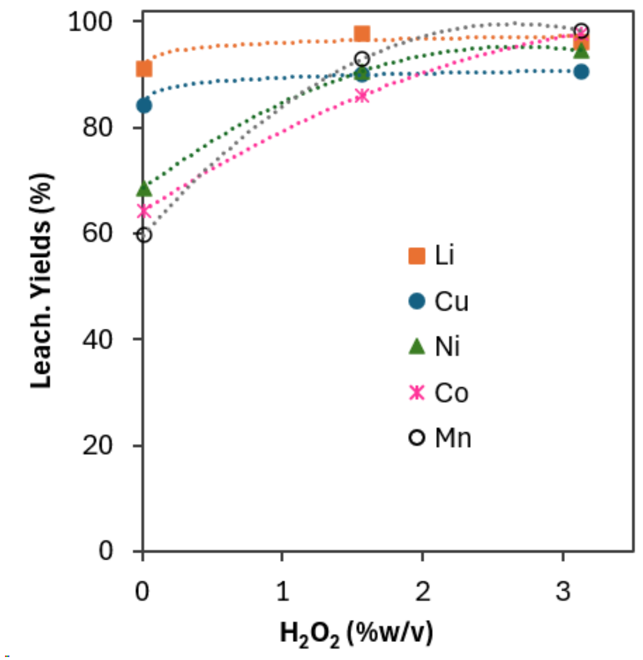
NCM-type cathodes of Li-ion batteries require reduction of Mn/Co/Ni to state 2+ to be soluble

Leaching of NCM-type black-mass with $Na_2S_2O_5$
(T = 60ºC, t = 1 h, H_2SO_4 = 0.75 M, L/S = 10 L/kg)



Highlights: Metals from the cathode material leach 80-90%
Reducing conditions depress copper dissolution

Leaching of NCM-type black-mass with H_2O_2
(T = 50ºC, t = 1 h, H_2SO_4 = 1.5 M, L/S = 10 L/kg)



Highlights: Metals from the cathode material leach 85-95%
Copper is also dissolved

Final remarks : Hydrometallurgy in Portugal

- Industrial hydrometallurgy projects have been operating in Portugal 40-50 years ago (zinc metallurgy in Barreiro, uranium processing in Urgeiriça);
- For several decades, projects of this nature were absent in our country;
- Currently, several hydrometallurgical projects are being evaluated, notably in the area of lithium metallurgy and battery recycling;
- In the PRR Agenda NGS – New Generation Storage, several actions and projects are being developed in several fields of the Li batteries value-chain, including extraction of raw-materials (Li) and recycling of spent Li-ion batteries

Action needed:

- Invest in the teaching and training of hydrometallurgy/extractive metallurgy at universities;
- Promote, continuously, industrial R&D actions and projects to assist companies in their productive investments

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Thank you

Acknowledgement

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New Generation Storage

PRR Plano de Recuperação e Resiliência

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