FRANCE 2030 PROGRAMME DE RECHERCHE RECYCLAGE

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LABORATOIRE DE GÉNIE CHIMIQUE
TOULOUSE ▪ UMR 5503

RECYCLAGE RECYCLABILITÉ RÉ-UTILISATION MATIERE PEPR

LULABAT
PROJET CIBLÉ BATTERIES

PEPR
Technologies Avancées & Analyses Socio-Economiques pour la Transition Ecologique dans le Recyclage

Towards the selective dissolution of lithium from NMC cathodes by leaching under oxidizing conditions

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3BCAR

Recycling of lithium-ion batteries : Context

PEPR Recyclage : LULABAT project

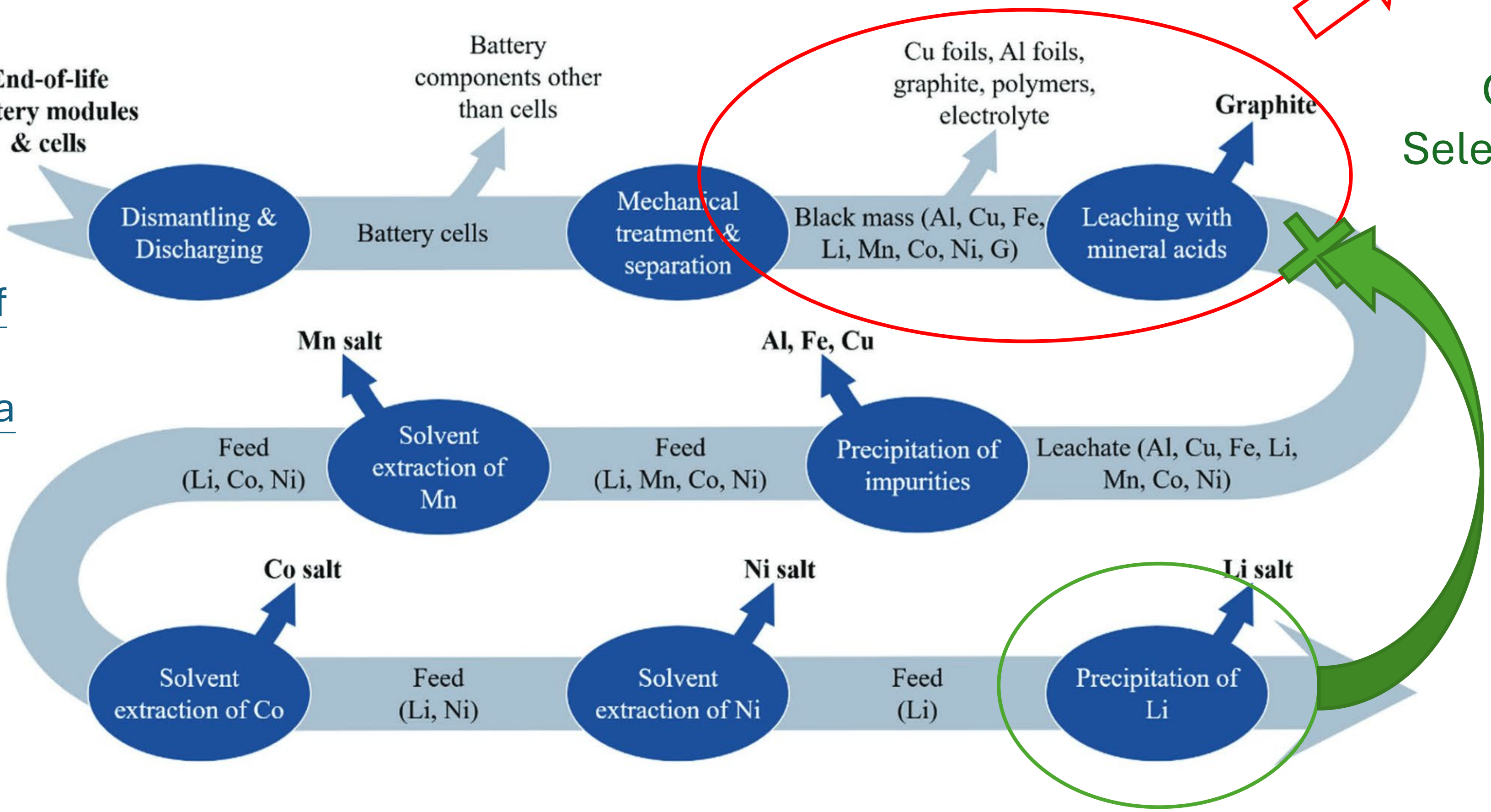
Main objectives of the LULABAT project:

- Graphite chain.
- Treatment of cathodes and recycling processes for used battery materials.
- Roberto Barbano, Grenoble
- Soukayna Badre-Eddine, Nancy

General objectives

Overview of a traditional hydrometallurgical process:

Principal steps of a traditional hydrometallurgical process [1]



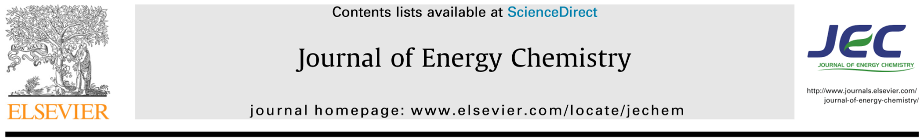
Thesis's field of study

Objective : Selective recovery of lithium

- ✓ Better yield
- ✓ Better selectivity
- ✓ Better process control and purification

[1] Neumann, Jonas, and al., Recycling of Lithium-Ion Batteries—Current State of the Art, Advanced Energy Materials vol 12-17 (2022)

State of the art: selective lithium extraction from spent lithium batteries


Contents lists available at ScienceDirect
Journal of Energy Chemistry
journal homepage: www.elsevier.com/locate/jechem

Review

Review of preferentially selective lithium extraction from spent lithium batteries: Principle and performance

Zhe Gao, Meiting Huang, Liming Yang *, Yufa Feng, Yuan Ding, Penghui Shao, Xubiao Luo *

4 main ways

- Electric energy
  - Direct redox
  - Mediated redox
- Chemical energy
  - Strong oxidizer
  - Deep-eutectic solvent, acid
- Mechanical energy
  - Isomorphic substitution
  - Direct redox
- Thermal energy
  - Direct leaching by calcination
  - Reagent assisted calcination

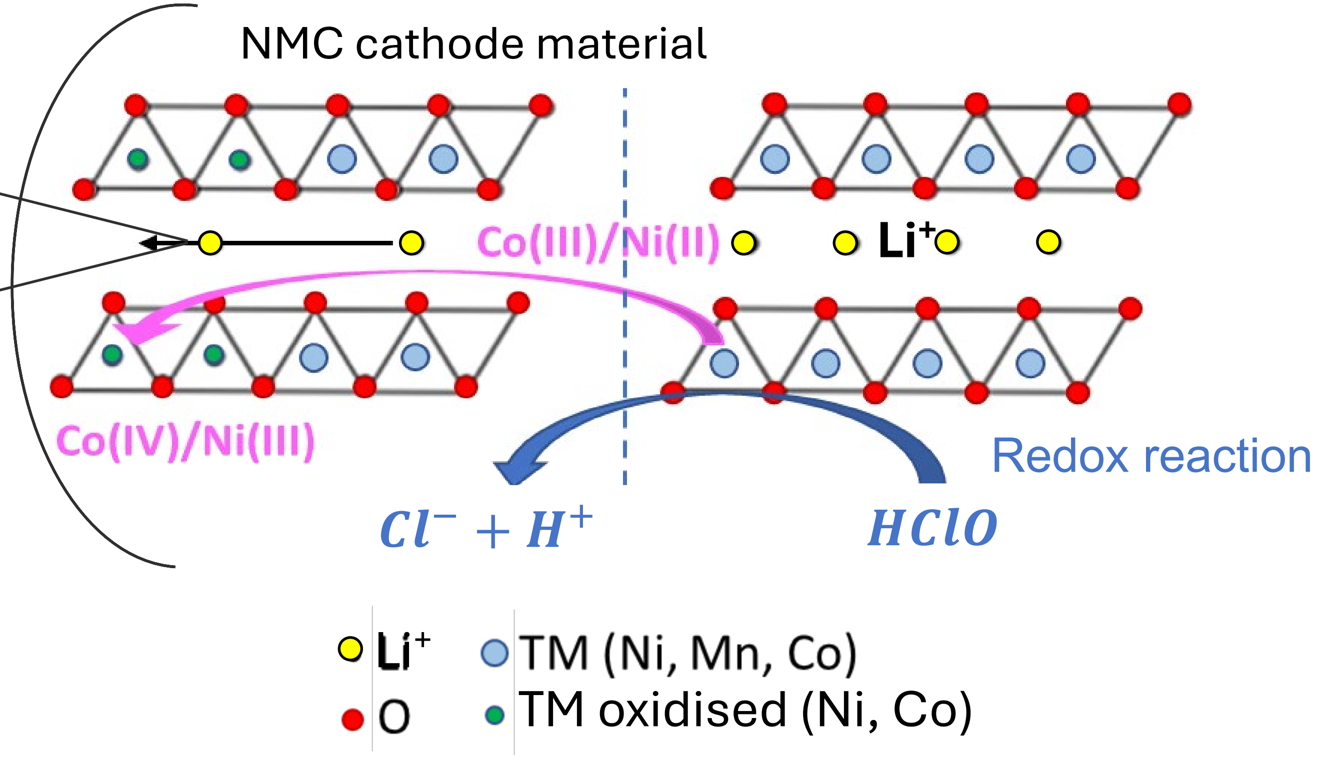


Diagram of the effect of the addition of an oxidant during leaching

[2] Z. Gao et al., JOURNAL OF ENERGY CHEMISTRY, vol. 78., p. 253-261, 2023
[3] Emmanuel Billy et al., ACS Applied Materials & Interfaces 2018 10 (19), 16424-16435

Aim of the thesis

ELSEVIER

Contents lists available at ScienceDirect

Separation and Purification Technology

journal homepage: www.elsevier.com/locate/seppur

Check for updates

Simple and efficient selective extraction of lithium from spent ternary lithium-ion batteries via oxidation/de-lithiation using NaClO

Yanhui Kong [a], Yutaro Takaya [b,d], Mauricio Córdova-Udaeta [c], Chiharu Tokoro [b,d,*]

- Oxidant: NaClO/Cl-
- Thermal pretreatment
- > 90% Li in best cases, 40-50% with other NMC materials/conditions

❖ What is the impact of the oxidative potential (Eh) on Li leaching (selectivity, yield)?

❖ Which phenomena limit the Li dissolution kinetics (shrinking core, surface passivation, chemical reaction, ...)?

❖ Does a variation of the BM composition have an effect on leaching efficiency?

[4] Yanhui Kong et al., Separation and Purification Technology, 2023

Methods: Raw material characterization before leaching

Black Mass characterization:

- 3 types of industrial BM from Sarpi-Veolia
- Stage 1: 4 steps samplings
- Stage 2: Implementation of an analysis strategy

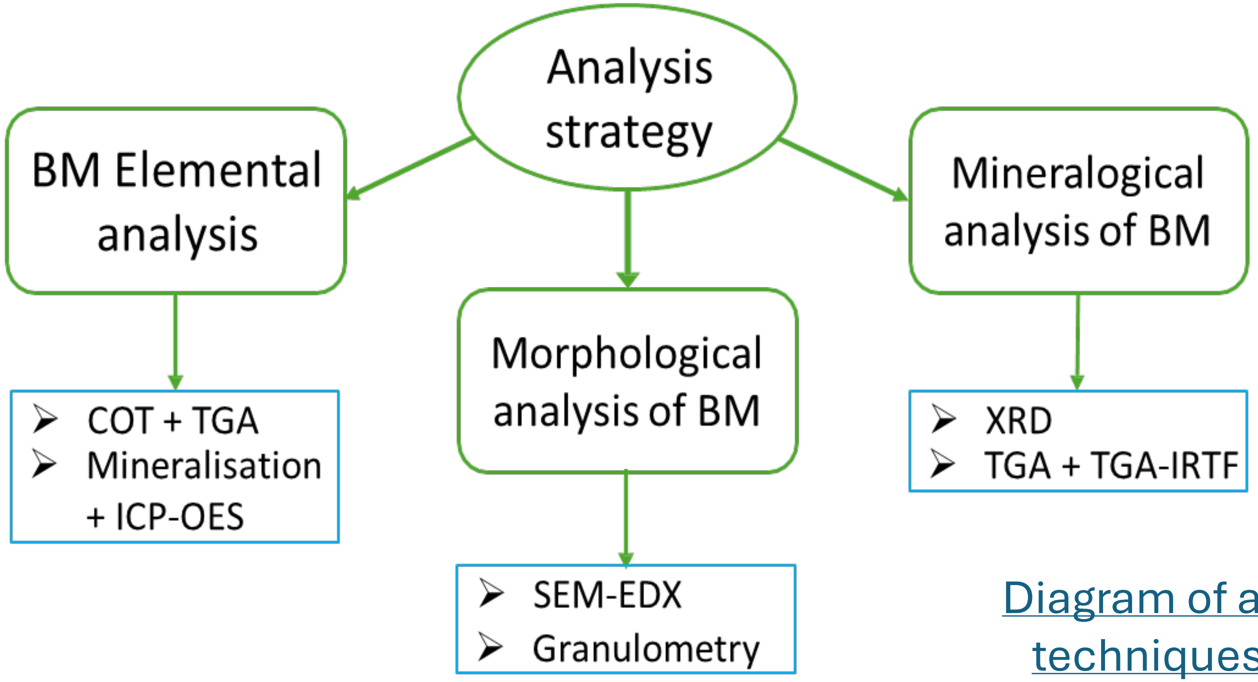
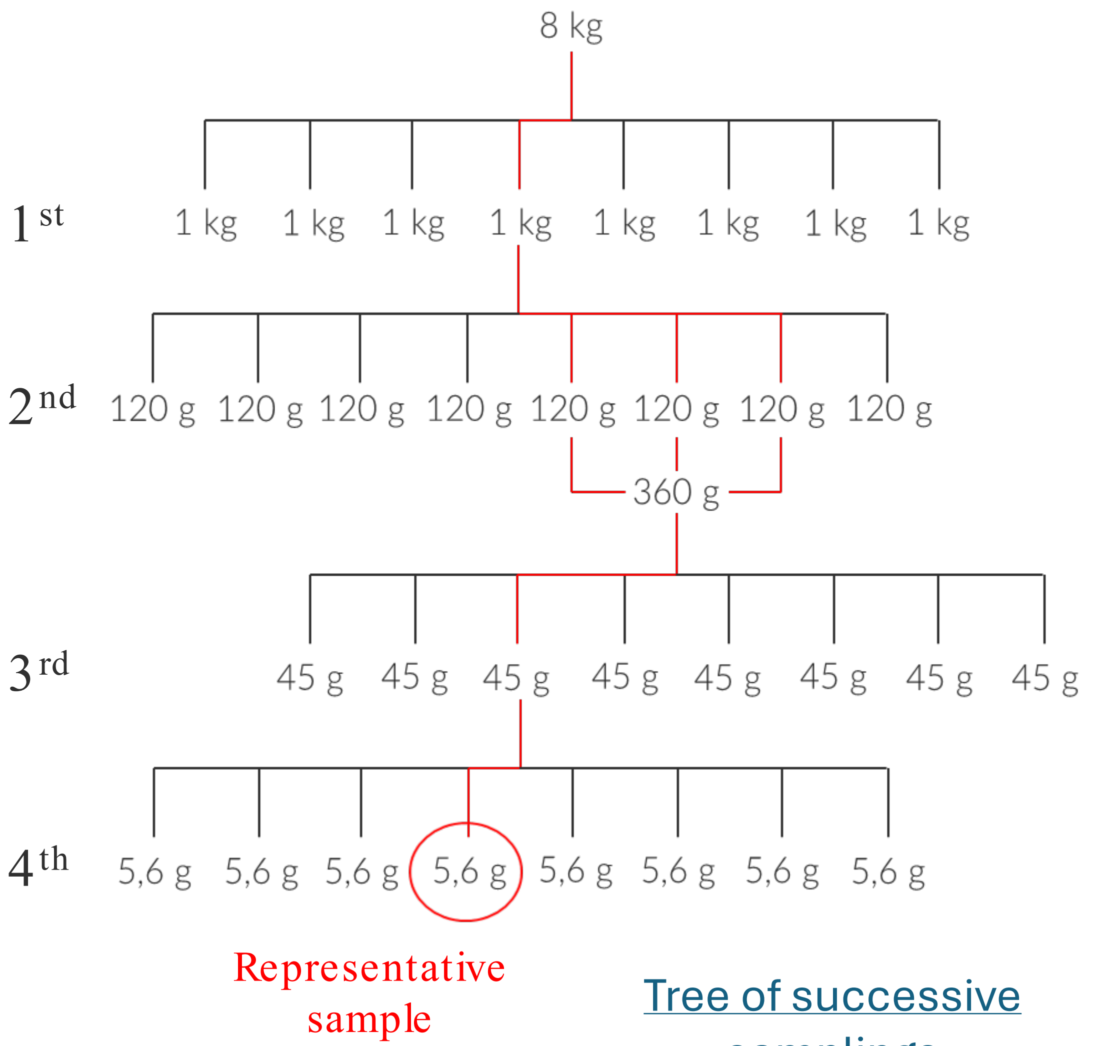
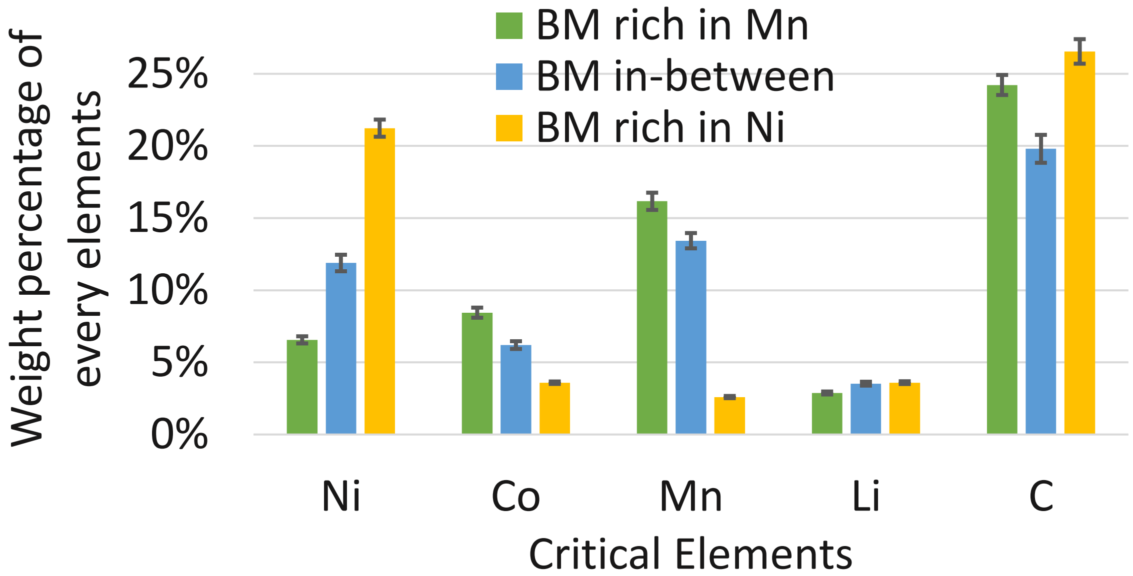


Diagram of analysis techniques used

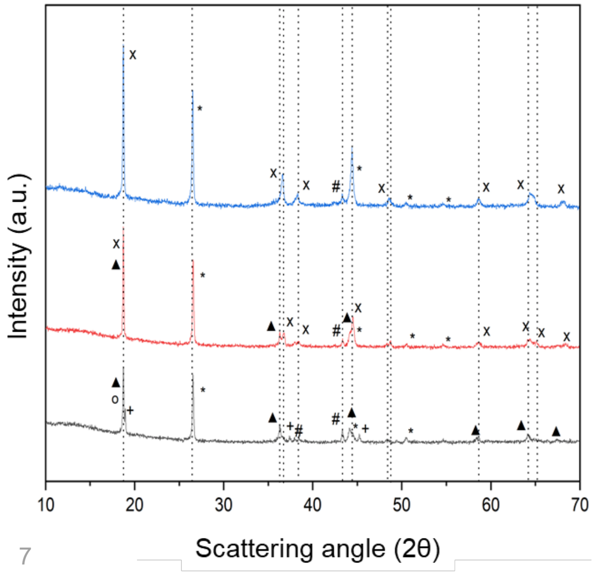


Tree of successive samplings

Results: Characterization of the industrial BM

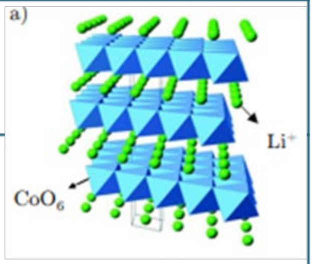
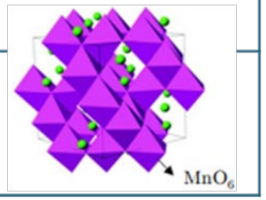


Elemental mass compositions of the 3 types of industrial BM from LiBs



Diffractograms of industrial BM

Examples of the crystalline phases that make up industrial BM

Sample	Crystalline lattice	Space group	a (nm)	c (nm)	Crystalline lattice of marketed materials [5]
BM rich in Ni	$Li_{0,96}Ni_{1,04}O_2$	R-3m (rhombo)	2,88	14,2	
BM in-between	$LiNi_{0,358}Mn_{0,358}Co_{0,283}O_2$	R-3m (rhombo)	2,87	14,3	
BM rich in Mn	$Li_{0,65}Mn_{2,08}O_4$	Fd-3m (cubic)	8,21	/	

[5] N. Nitta, F. Wu, J. T. Lee, and G. Yushin. Li-ion battery materials: present and future. Materials Today, 2015

Methods: Leaching pilot

Leaching study methodology:

Experimental conditions:

- pH and Eh regulation:

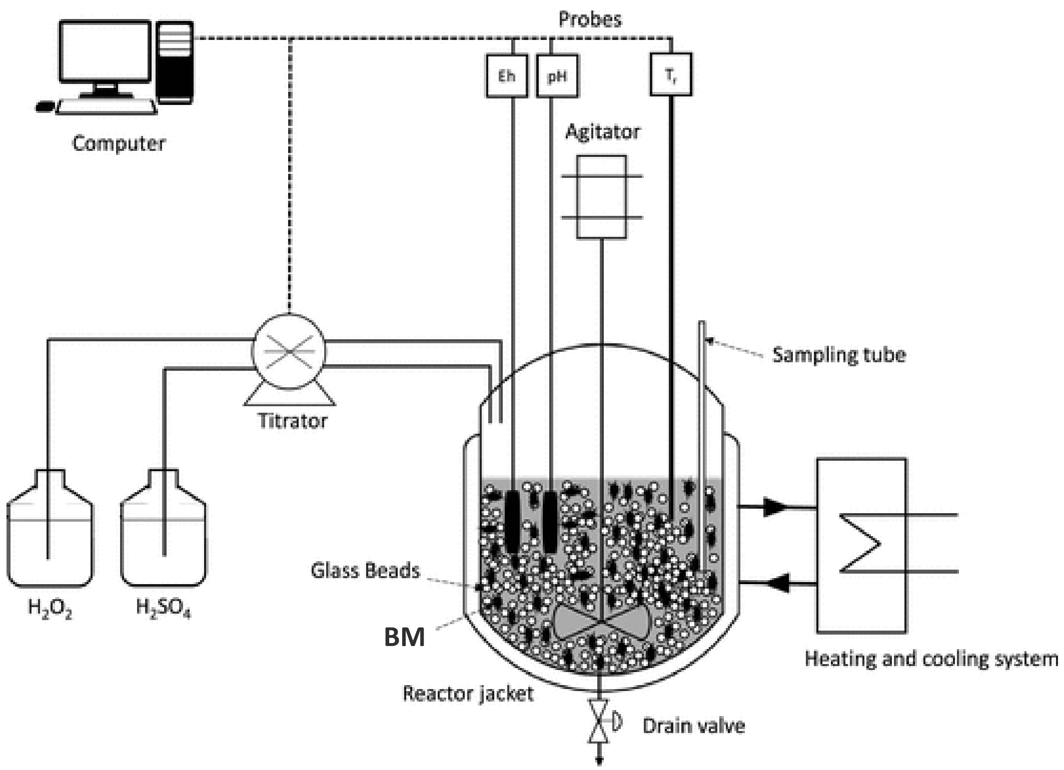
-> Kinetic monitoring of leaching progress:

  - Acid consumption
  - ICP analysis of suspension samples taken during the reaction.

- Leaching:

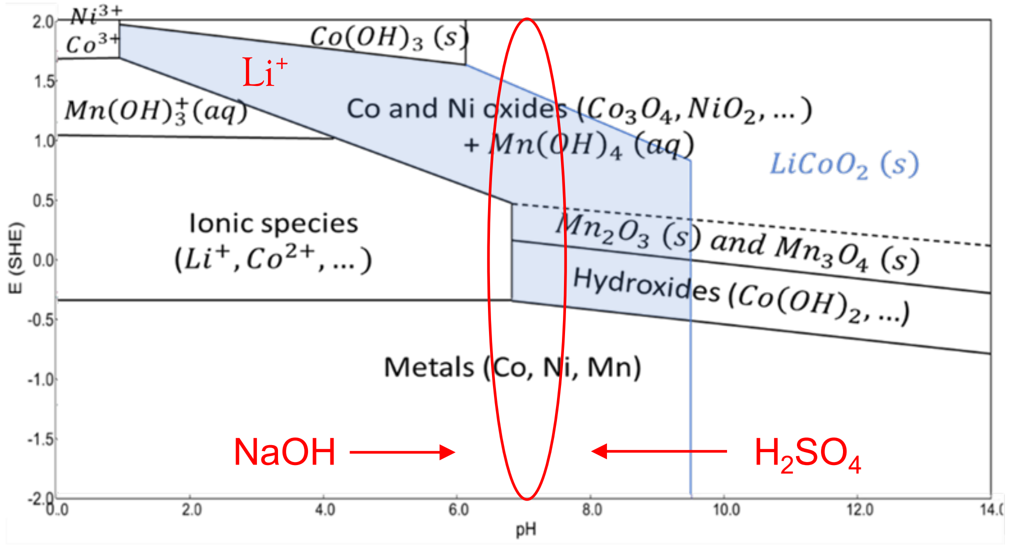
-> pH from 6 to 9

-> Eh from 450 to 1140 mV vs ESH

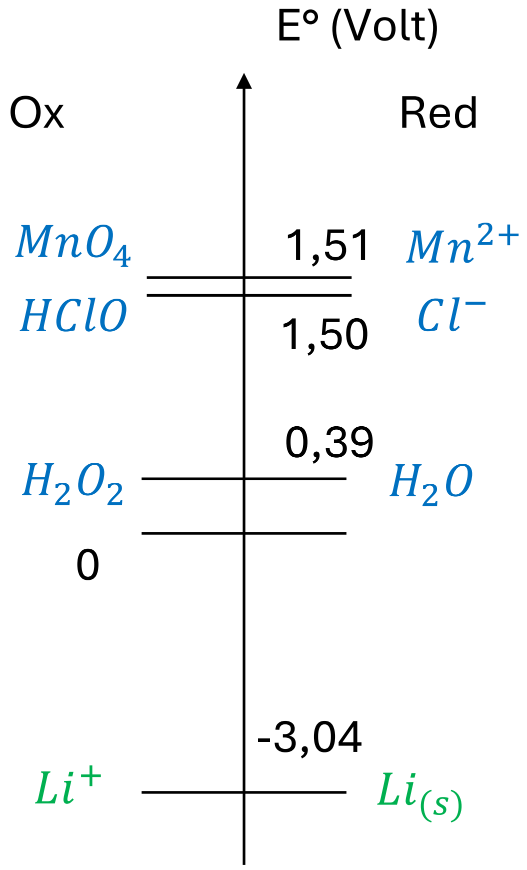


Methods: Leaching experimentations under oxidizing conditions

- Regulation of the pH, between 6 and 9 :



Dominant species for the leaching of a typical BM as a function of pH and Eh (OLI Studio simulation)



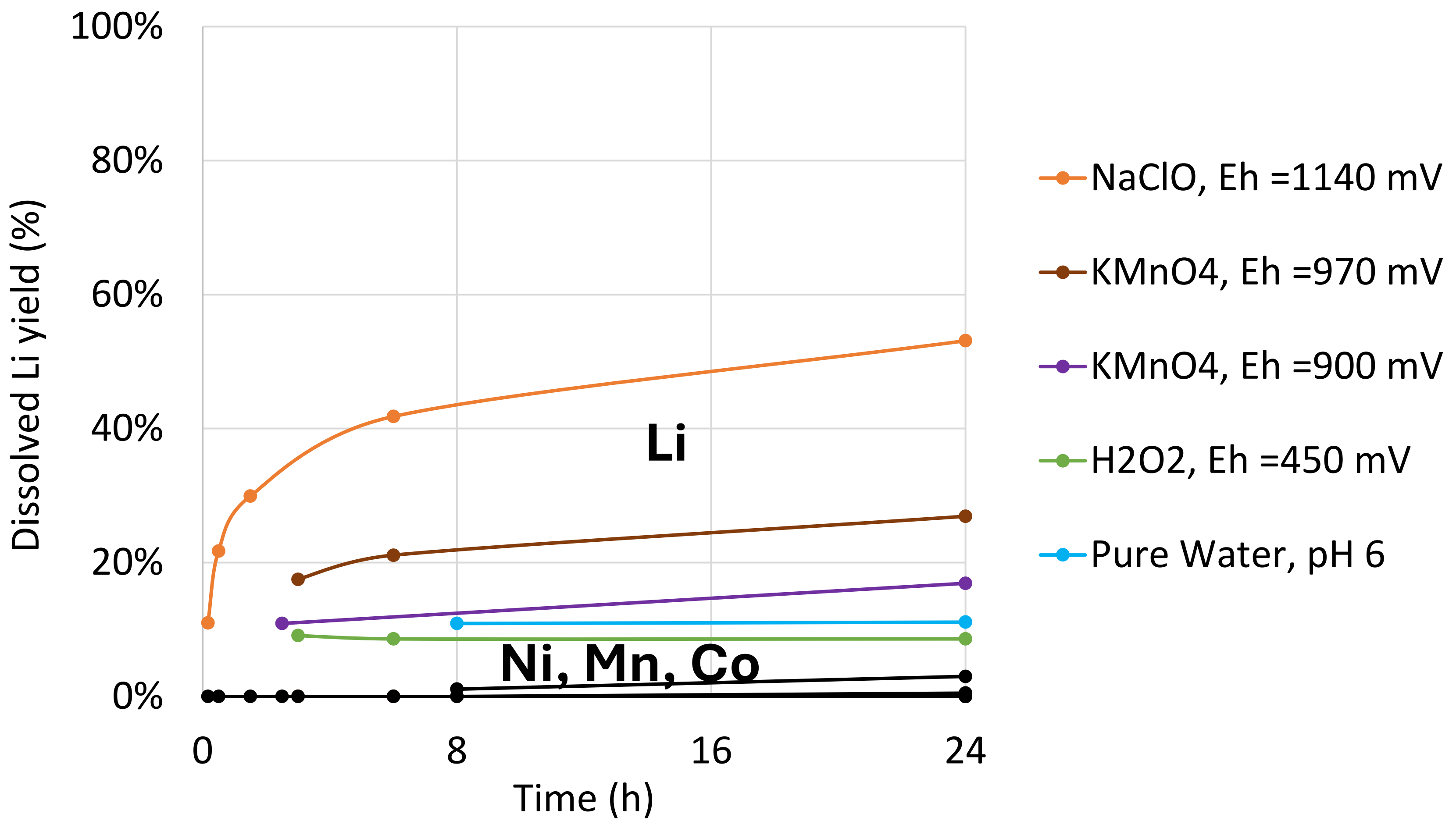
Scale of standard redox potentials

- Leaching with different strong oxidants:
  - -> H_2O_2, no additional element
  - -> $KMnO_4$, + K and Mn
  - -> NaClO, + Na

[6] Willem H. Koppenol et al., Free Radical Biology and Medicine, Volume 49, Issue 3, 2010, Pages 317-322

Results: Effect of redox potential

Monitoring of dissolved lithium yield during leaching at pH 7 with controlled addition of oxidants

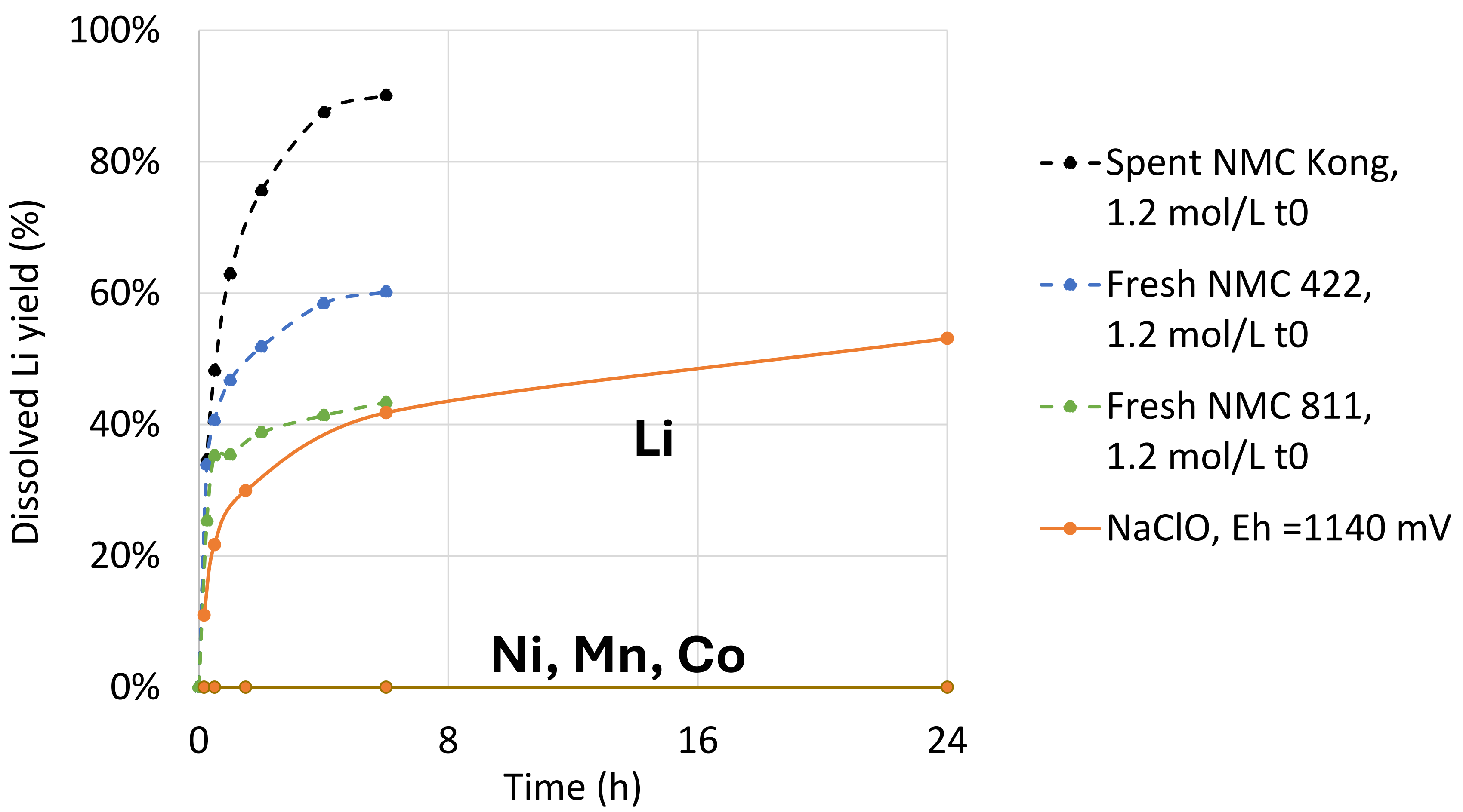


- 10 % Li leaching in pure water at pH 6.
- No effect of H_2O_2.

- Delithiation is more effective at higher redox potentials.
- High Li selectivity vs Ni, Mn, Co.

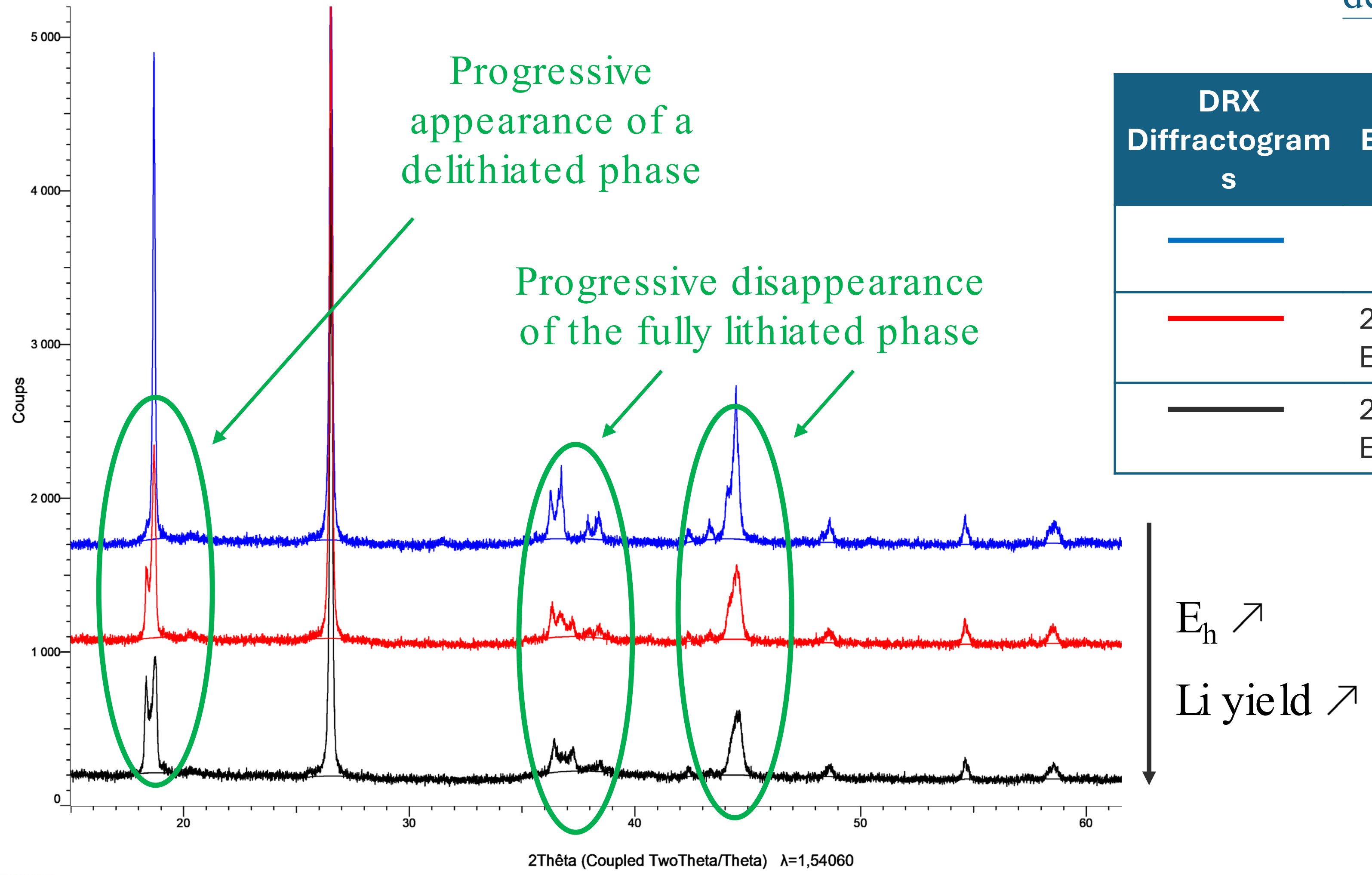
Results: Effect of redox potential

Comparison of dissolved lithium yield during leaching at pH 7 and Eh = 1140 mV between experimentation and Kong et al. results [4]



- Kong's leaches in NaClO concentrated solution.
- A higher concentration leads to a faster delithiation.
- Results similar Fresh NMC/experimentation.
- Lithium selectivity towards the NMC phase.

Results: X-ray diffractograms of solid residues



Evolution of crystalline phases during delithiation using XRD analysis

DRX Diffractograms	Echantillon	Crystal Structure	Space group	x in Li_xMO_2	Scattering angle (2θ)
(blue line)	Industrial BM	O3	R-3m	1	18.6
(red line)	24h, KMnO4 Eh = 900 mV	O3'	C2/m	0.5/0.6	18.4
(black line)	24h, KMnO4 Eh = 970 mV	H13	R-3m	0.5	18.4

Evolution of the phases making up the intermediate BM as a function of the lithium yield

Results: Effect of grinding beads on the selective leaching of lithium

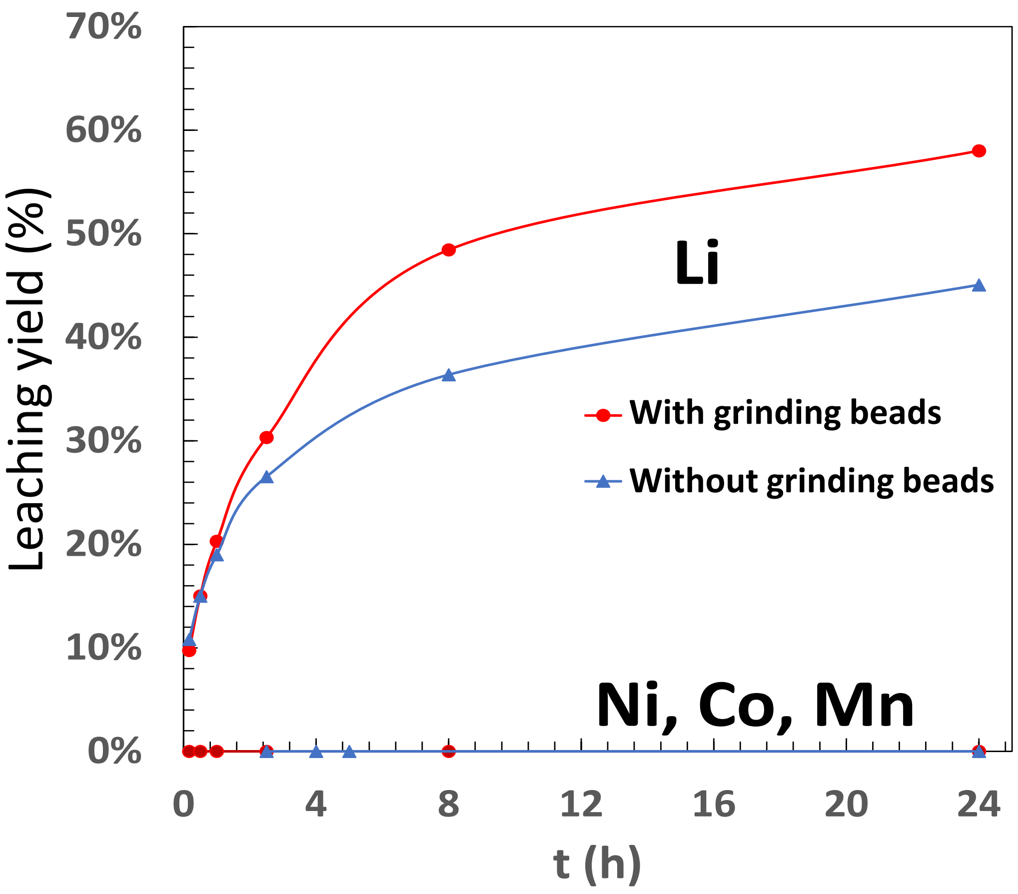
<u>Conditions :</u>

- pH regulation set at 7 by adding 1 M H_2SO_4.
- E_h monitoring, excess $KMnO_4$, with and without grinding beads.
- Grinding beads: glass beads, 500 g, diameter = 1.3 – 1.7 mm.

Material balances for the various leaching processes carried out with excess oxidant

Leaching	Dissolved Li yield (%)	n_Li dissolved (moles)	n_H_2SO_4 (moles)
Excess of KMnO4, without beads	45,0%	0,12	0,09
Excess of KMnO4, with beads	58,0%	0,15	0,11

➢ Moderate effect of glass beads.



Monitoring of H_2SO_4 consumption for a pH maintained at 7 by controlled addition with and without beads

4 key conclusions

- Achievement of >50% fully selective Li dissolution with $KMnO_4$ and NaClO oxidant

- Delithiation yield increases with E_h

- Delithiation forms new Li-depleted phases

- Mechanical effect (grinding, attrition) of glass beads is limited, showing that the reaction kinetics is not strongly hindered by the neo-formed phases

Thank your for listening !

Any questions ?