EXPERIMENTAL STUDIES ON ACID LEACHING OF EV BATTERY PRODUCTION SCRAP

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LI-ION BATTERY AND CHALLENGES

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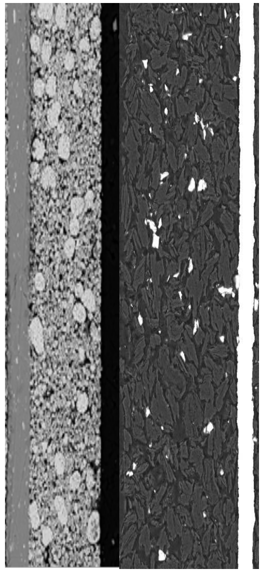
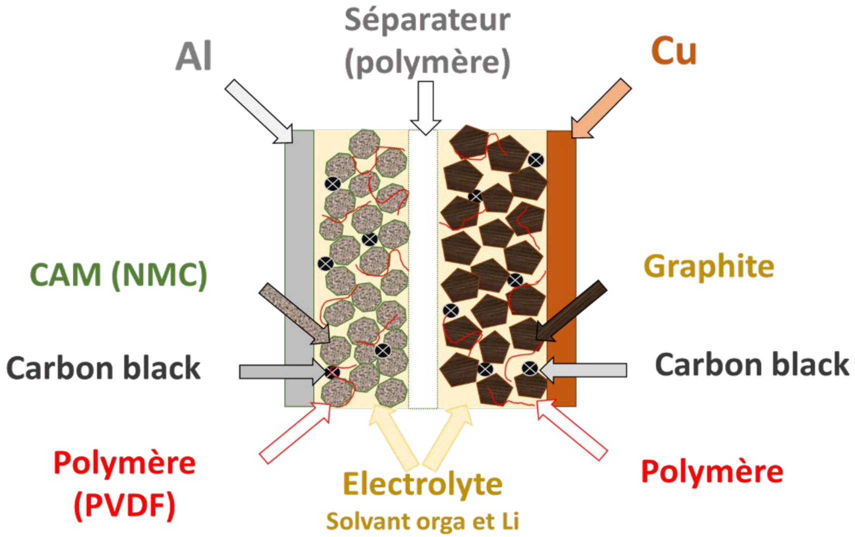
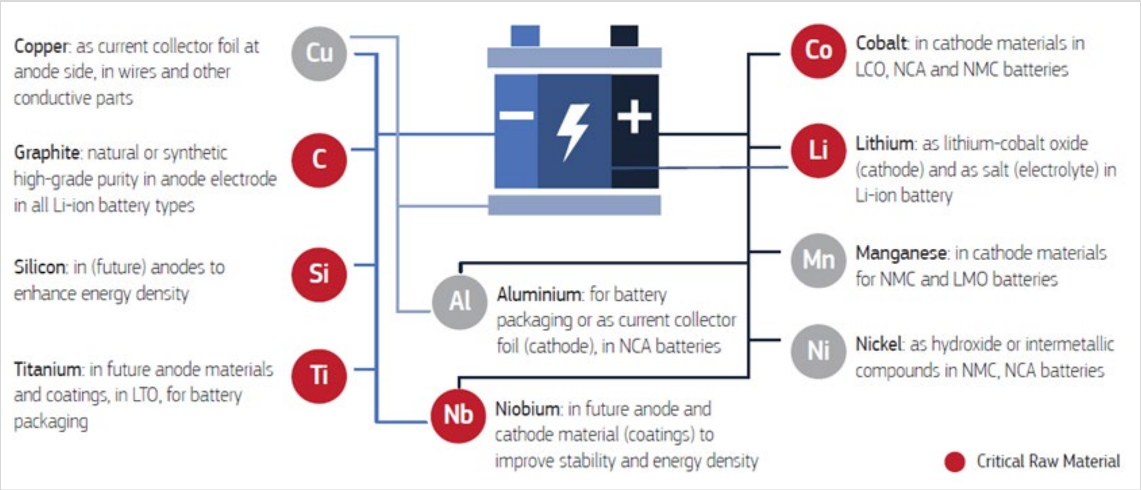
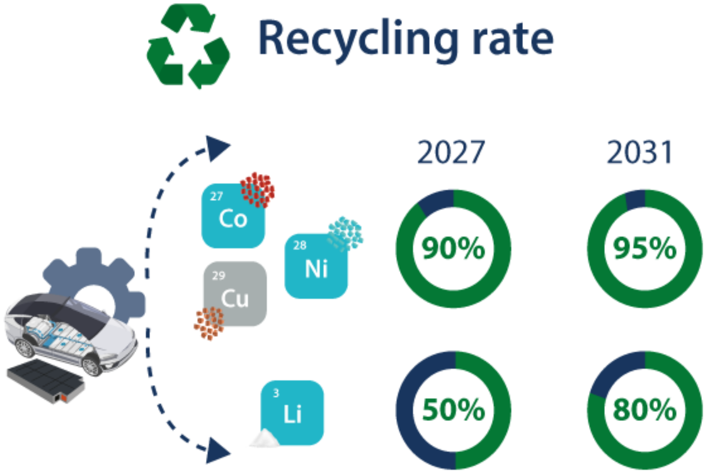
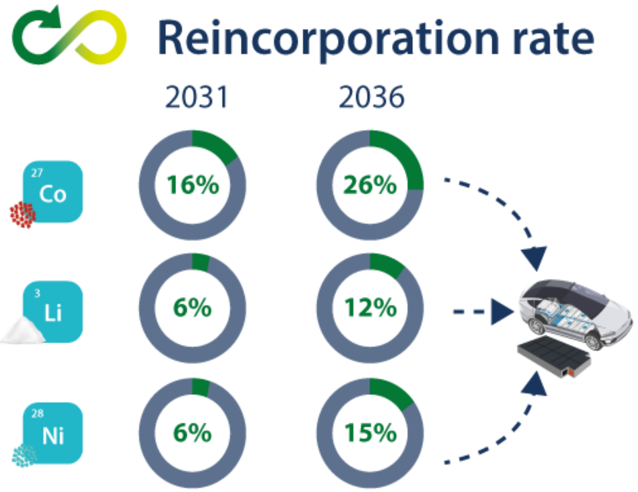






Critical éléments in batteries





PROCESS

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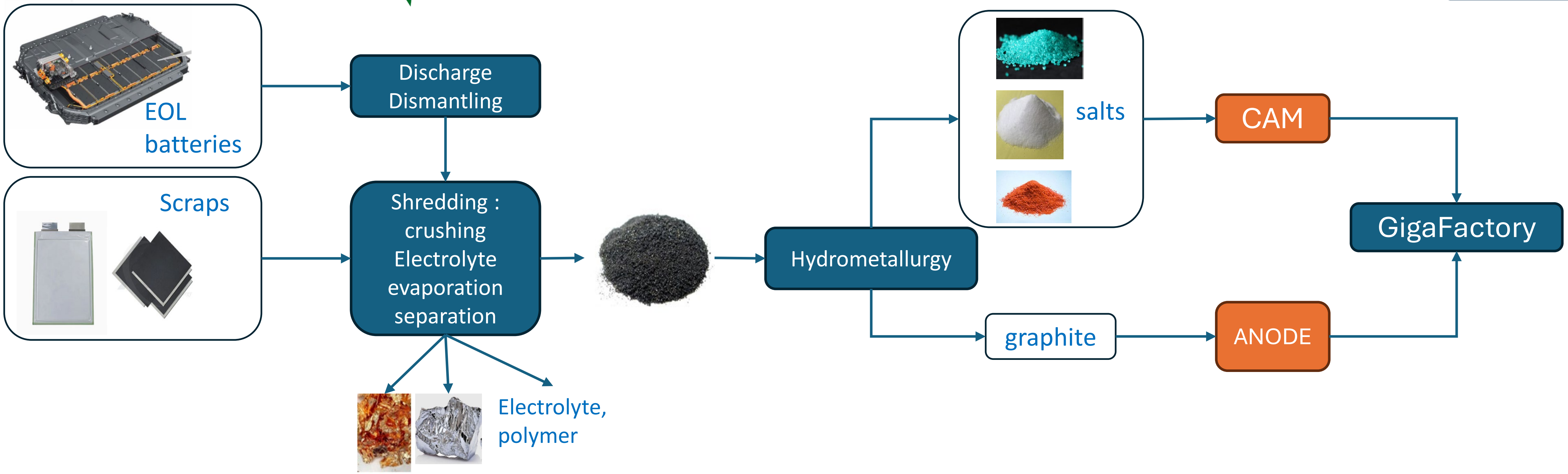

RECORD : SECOND GENERATION RECYCLING PROCESS

LOWER CO2 EMISSIONS – LOWER CAPEX – CLOSING LOOP MAXIMIZATION

Duration : 7 years

- BM Conditioning
- Primary Delithiation on BM
- Co Extraction
- pCAM integration
- Na_2SO_4 recycling
- ACV Simulation Thermo

PRELIMINARY RESULTS

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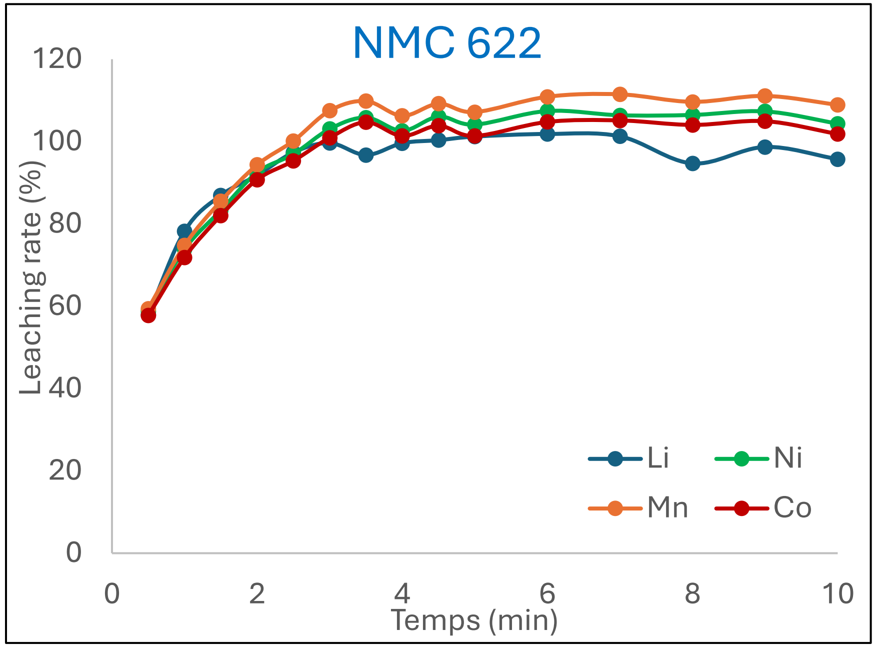
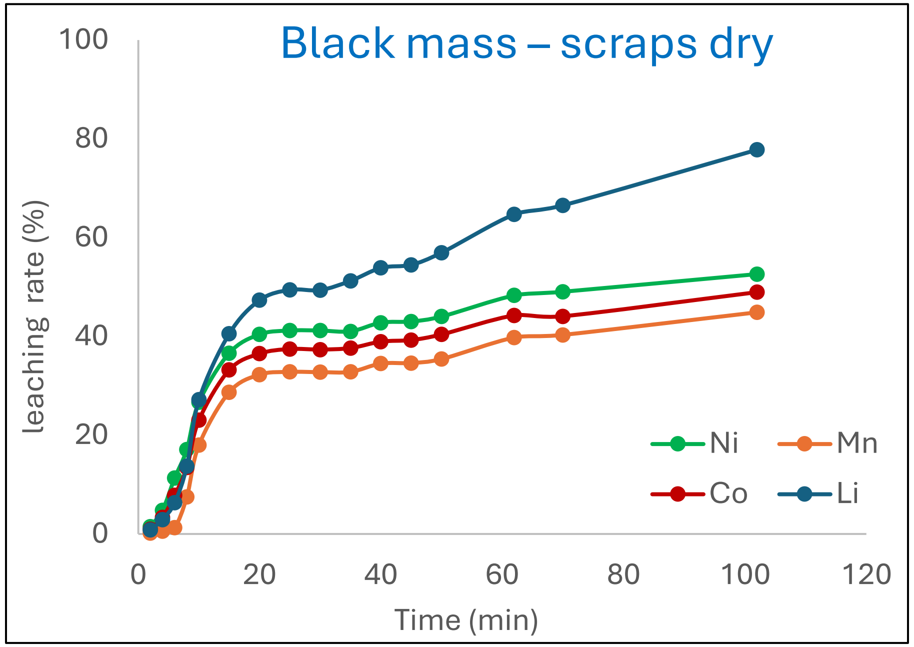
Materials:

- Volume: 200 ml
- Leaching agent: 1.5 eq of H_2SO_4
- Reductive agent: H_2O_2
- Ratio L/S = 15
- Temperature = 50 °C

Leaching reaction:

$$5\ LiNi_{0,6}Mn_{0,2}Co_{0,2}O_2 + \frac{15}{2}\ H_2SO_4 + \frac{5}{2}\ H_2O_2 \rightarrow 3\ NiSO_4 + MnSO_4 + CoSO_4 + \frac{5}{2}\ Li_2SO_4 + 10\ H_2O + \frac{5}{2}\ O_2$$





- Leaching depending on material ➔ experiments on industrial BM
- Analysis of BM and experiments at pilot scale
- Goal : understanding impact of impurities on leaching and kinetic modelling

OVERVIEW OF HYDROMETALLURGICAL RECYCLING

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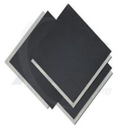
Mobilité durable

- Hydrometallurgical processing relies on transferring valuable metals from spent LIBs into a solution (leaching), followed by separation and extraction to obtain either single metal compounds or mixtures of them.
- The industrial source of valuable metals from battery production or spent batteries called **black mass**.

Black Mass (NMC)

EOL batteries

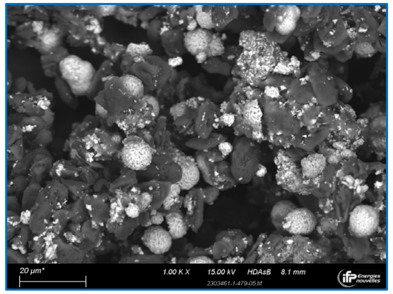


Scraps

- Discharge
- Dismantling
- Crushing
- Sieveing

Anode: graphite
Cathode: LiNiMnCoO2 (NMC)
Collectors: Al, Cu foils
Casing: Fe
Binders: PVDF
Coatings: Al_2O_3 ou AlOOH, TiO_2, ZrO_2 ou Li_2ZrO_3

Elements	
Majors	Li, Ni, Mn, Co, graphite
Minors	Cu, Al, Fe, PVDF



The challenge is a black mass with a stable quality and a low impurity content

Leaching → **Graphite, Polymère**

↓

Purification → **impurities Fe, Cu, Al**

↓

Extraction Séparation Purification → **Na2SO4**

→ **NiSO4, MnSO4, CoSO4, LiOH or LiCO3**

Leaching (dissolution) is a key step in the whole hydrometallurgical process
Working with a real feed is crucial – impurities impact on leaching efficiency

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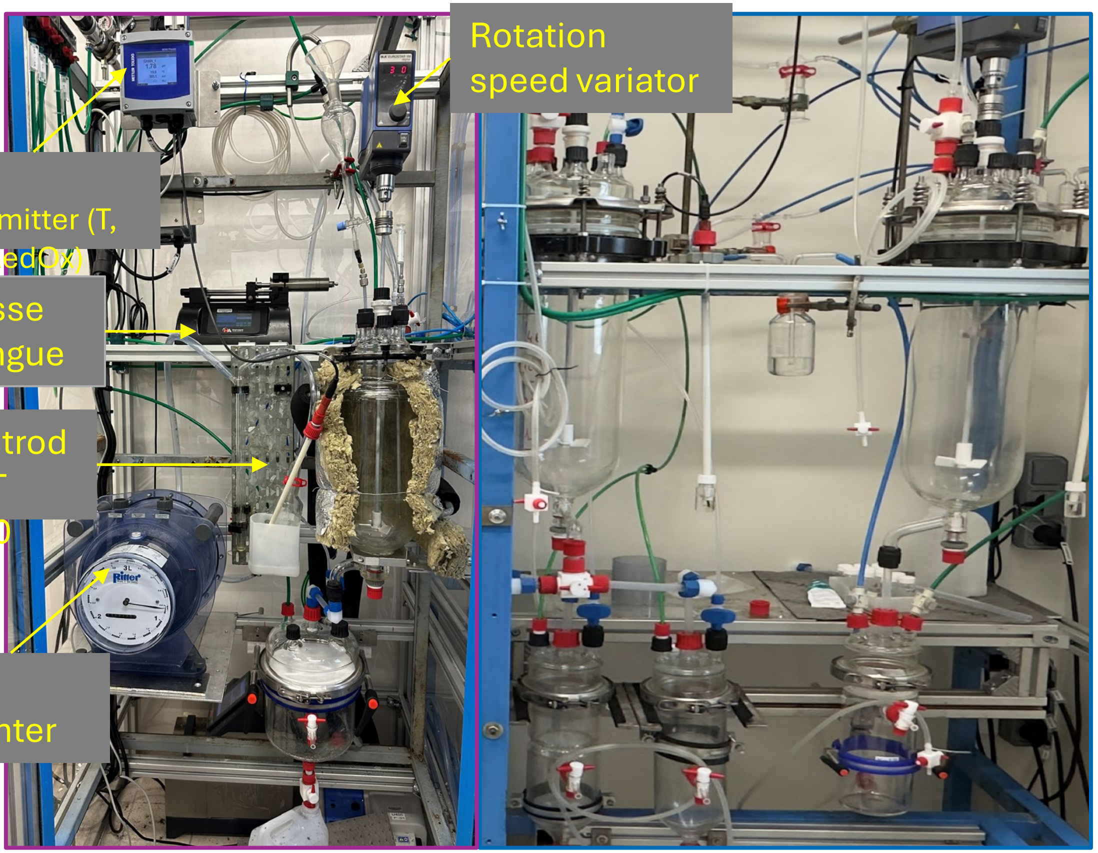
MATERIALS AND METHODS

Experimental set-up:

R1 – 5 L D.J. (Leaching) → R2 - 10 L (Precipitation) → R3 – 12 L (Precipitation)



- Peristaltic pump
- Vacuum oven

Leaching reaction: $5\ LiNi_{0,6}Mn_{0,2}Co_{0,2}O_2 + \frac{15}{2}\ H_2SO_4 + \frac{5}{2}\ H_2O_2 \rightarrow 3\ NiSO_4 + MnSO_4 + CoSO_4 + \frac{5}{2}\ Li_2SO_4 + 10\ H_2O + \frac{5}{2}\ O_2$

Materials:

- Black mass: NMC type 622, 111, 811 (EOL or production scraps)
- Leaching agent: H2SO4
- Reductive agent: H2O2
- NaOH for precipitation (R2 and R3)

Leaching protocol (batch mode):

- Consecutive injections: acid > BM > peroxide
- t = 3 - 5 h, T = 50-90°C, atm pressure,
- Filtration, washing, drying, grinding

Analysis:

- Solids: CHNOS (for carbon black quantification), XRF, ICP (Li), SEM, Laser Diffraction
- Liquids: ICP-OES

RESULTS

Results of 3 leaching tests using production scrap black mass NMC622

	rpm	H2O2 injection point	n H2O2 injecté	n H2O2 réagi	nH2O2/ nNMC	S/L ratio	Ni	Mn	Co	Li	Cu	Al	Fe
EXP005	300	interface	0,7		1,09	171	81%	70%	81%	89%	82%	13%	55%
EXP006	**500**	interface	2,1		**3,27**	**153**	96%	93%	96%	99%	96%	23%	77%
EXP007	500	**impeller**	2,1	0,67	3,27	153	**99,6%**	**99,6%**	**99,6%**	**in process**	**100%**	**28%**	**100%**

- Mass balance challenges due to black mass homogenity are adressed>> sampling uncertainty for BM and leaching residu was examined
- XRF analysis showed low uncertainty >> defined as a truthpoint for this tests

Complete leaching was achieved (objective > 95%) except for Al

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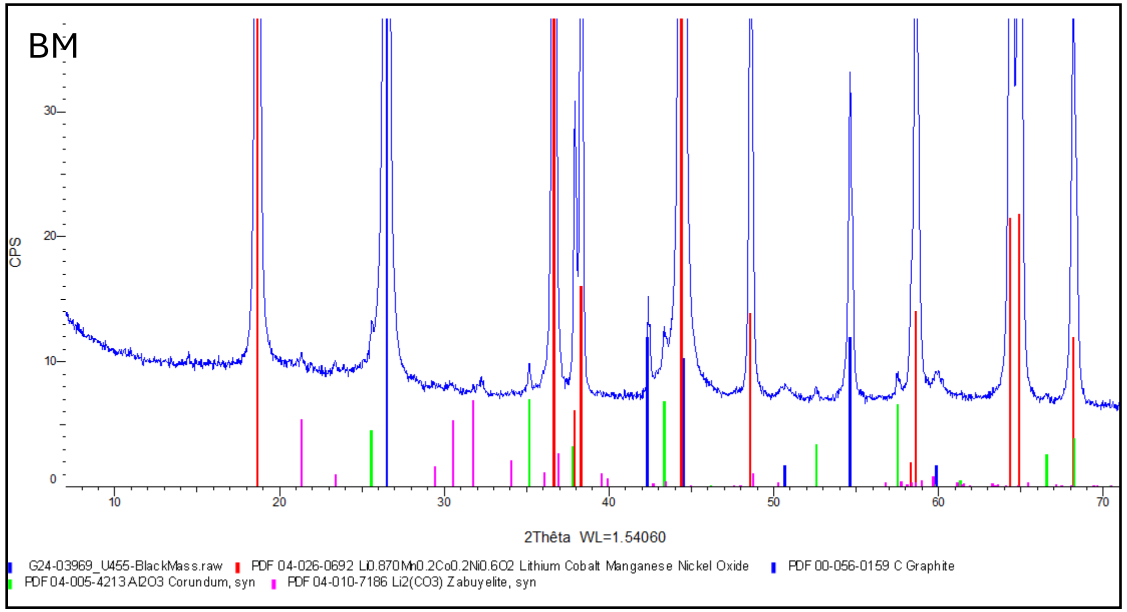
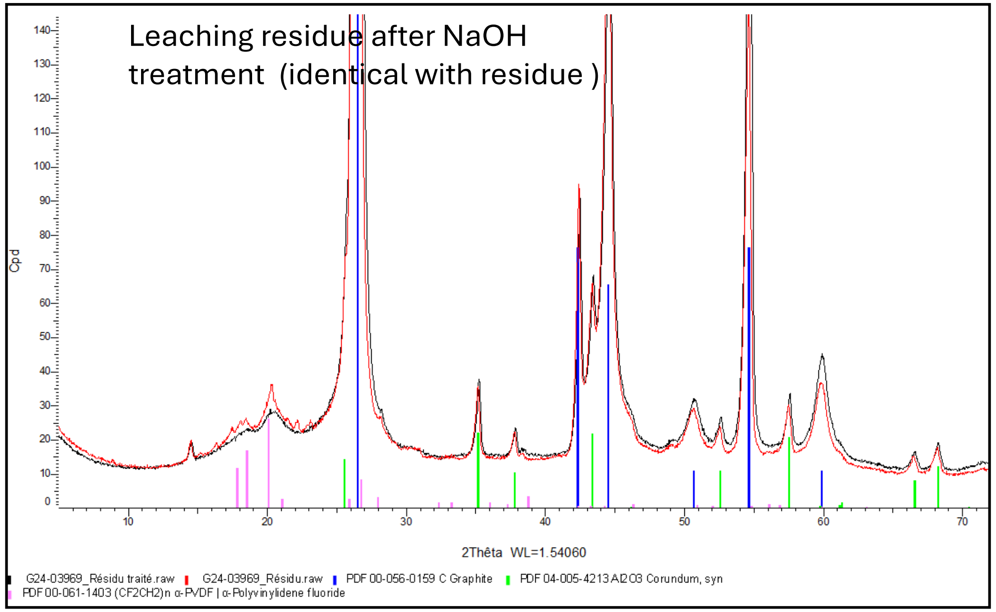
ALUMINIUM DISSOLUTION (EXP 007)

Poor dissolution of Al can be related to Al2O3 alpha. Where it comes from? Is it initially presented in BM due to coating or it forms due to lixiviation?

Approach: leaching residu alkali leaching





- α-Al_2O_3 is initially present in the black mass and persists to acid and alkali leaching
- Alkali leaching did not yield supplementary Al dissolution (confirmed by ICP IOS and XFX results) > entire gamma Al was recovered by acid leaching
- No NMC detected in leaching residu >> confirms complete dissolution

CONCLUSIONS

- Achieved recovery efficiencies > 99% for Cu, Fe, Ni, Co, Mn and Li
- Aluminum leaching remains challenging (28%) due to the stable Al_2O_3 corundum phase
- Pilot unit is qualified for leaching and precipitation studies

ON GOING STUDIES - EXPERIMENTAL STUDY ON LEACHING KINETICS

- 15 tests with different industrial black mass
- Studies of transfer limitations
- Impact of operating conditions (C_{acid}, C_{red}, T, S/L ratio) and impurities
- Development of grain model to describe kinetics of leaching and consider the speciation of species in solution

Innover les énergies

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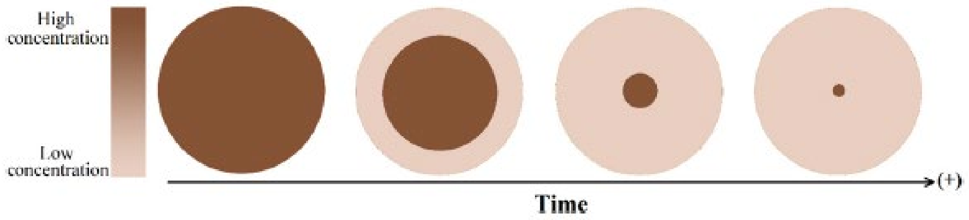
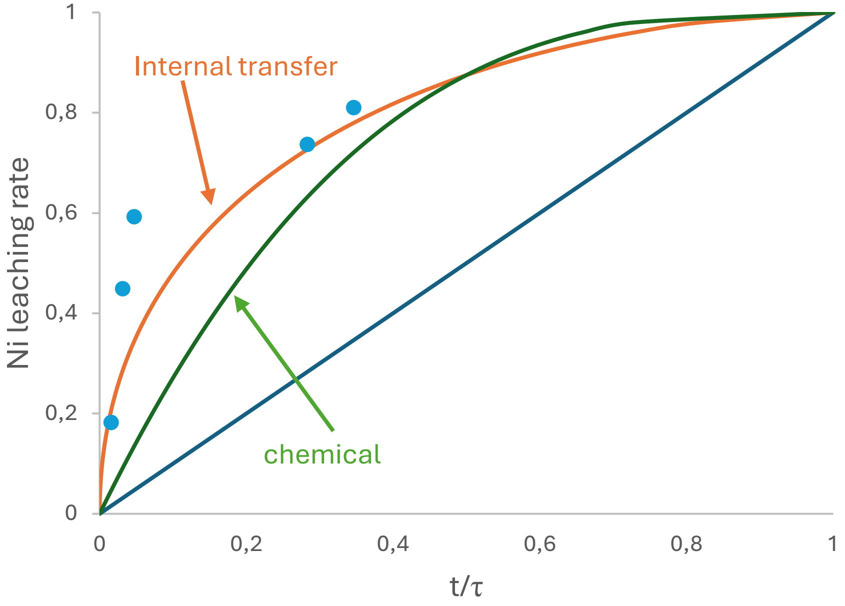
ON GOING STUDIES - EXPERIMENTAL STUDY ON LEACHING KINETICS

- **Shrinking core model** $A_f + \nu\, B_s \longrightarrow products$



- Non-porous spherical particules
- Order 1 (liquid phase) and independent of solid concentration: $r = k\, C_e$
- C_e , C_b ($C_B = \frac{\rho_B}{M_B}$) and T constants

	External transfer	Internal transfer	chemical
sphere $X_b = 1 - \left(\frac{R_c}{R_0}\right)^3$	$\frac{t}{\tau_{ext}} = X_b$	$\frac{t}{\tau_{dif}} = 1 - 3(1 - X_b)^{\frac{2}{3}} + 2(1 - X_b)$	$\frac{t}{\tau_{chim}} = 1 - (1 - X_b)^{1/3}$



- Non-porous grain model verification test (test duration variation)
- L/S external diffusion limitation test (agitation speed variation)
- L/S internal diffusion limitation test (granulometry variation)
- H_2SO_4 reaction order determination (acid concentration variation)
- H_2O_2 reaction order determination (H_2O_2 concentration variation)
- Activation energy determination (temperature variation)
- C_{NMC} reaction order determination (solid/liquid ration variation)

