

Process-Oriented Characterisation of Black Masses for Adaptive Circular Hydrometallurgical Processing

Michèle BATUTIAKO¹

¹GeMMe - Mineral Processing and Recycling, Faculty of Applied Sciences, University of Liège, Belgium
m.batutiako@uliege.be

GeMMe
Georesources, Mineral Engineering
& Extractive Metallurgy

LIÈGE université
Urban & Environmental
Engineering



BLACK MASS CHEMISTRY ALONE IS INSUFFICIENT TO ANTICIPATE ITS HYDROMETALLURGICAL BEHAVIOUR...
Hence... which other black mass characteristics are relevant to anticipate this behaviour?

1 Why look beyond bulk chemistry?

Industrial black masses inherit both battery chemistry and upstream processing history. The bulk elemental analysis defines the feed inventory but does not indicate the speciation nor the particle-scale state in which the elements enter the hydrometallurgical processing.

This work screens bulk, phase- and particle-scale signatures across multiple industrial black masses against hydrometallurgical behaviour to identify candidate process-relevant descriptors for upstream process optimisation, downstream response interpretation and future prediction.

Materials

9 investigated industrial black masses

- 3 Mechanical (M1, M2, M3)
- 3 Thermomechanical (TM1, TM2, TM3)
- 2 Vacuum (V1, V2)
- 1 Atypical (A1)

Methods*

Bulk chemistry
ICP-OES | XRF | C_{tot}

Phase state
SEM-EDS | Auto.
Mineralogy

Particle state
PSD + ICP-OES | Auto.
Mineralogy

* Main, non-exhaustive

2 Because of variable industrial feeds

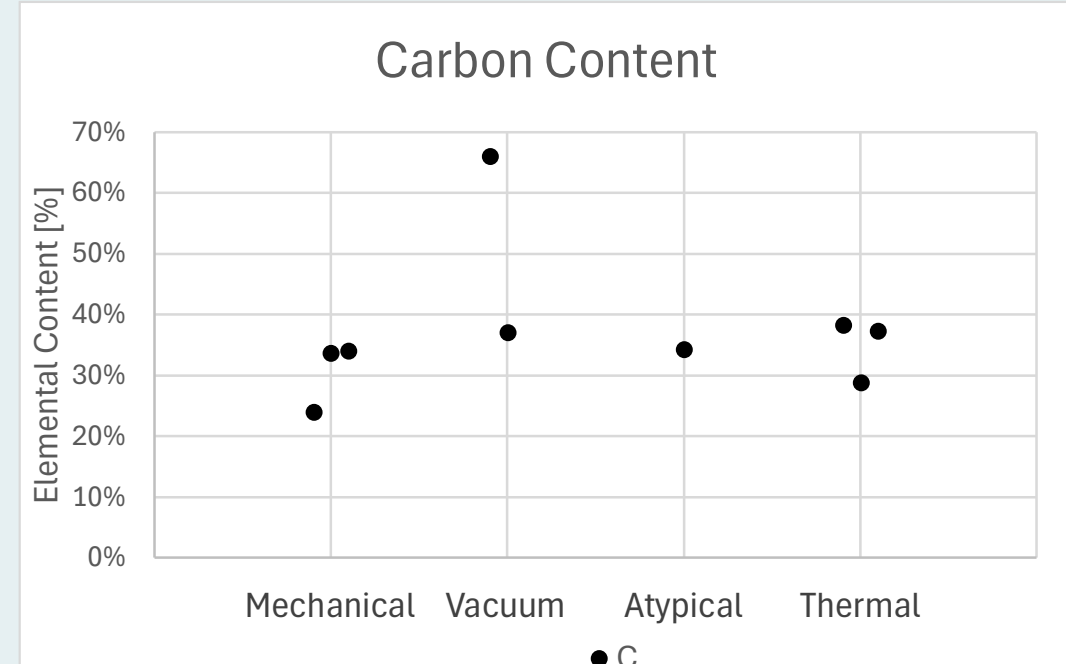
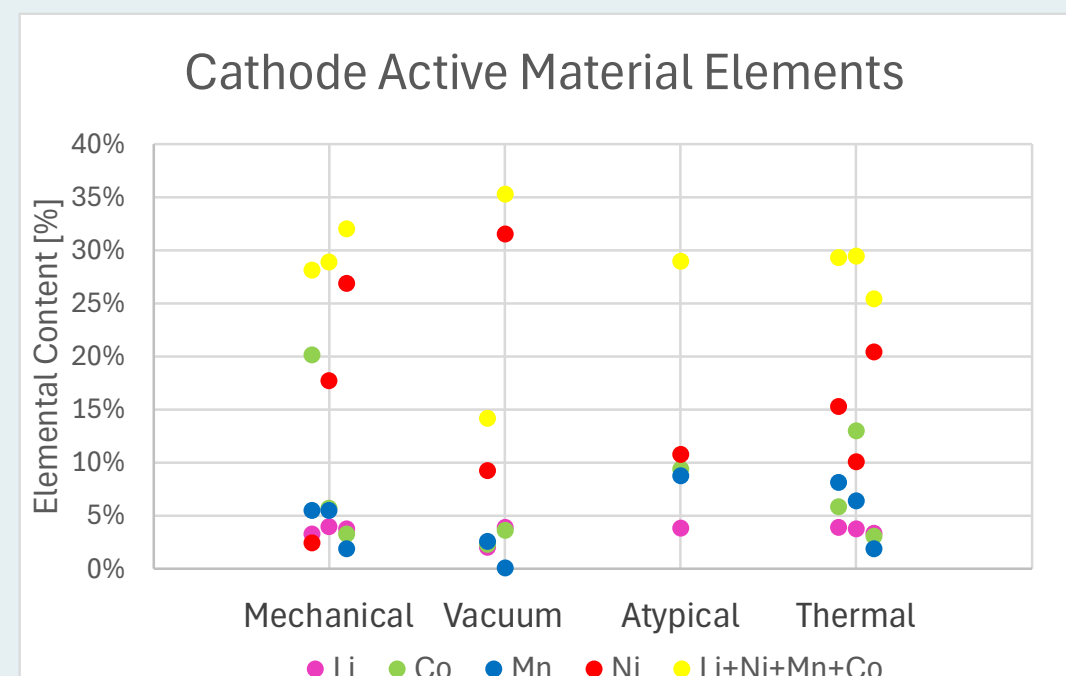
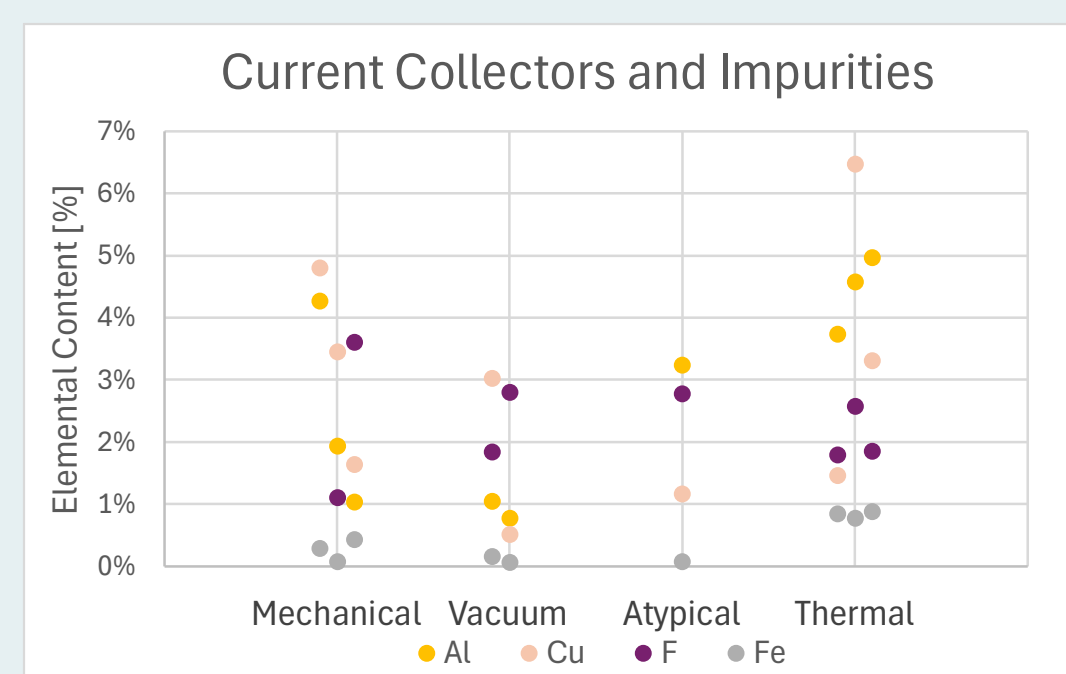


Figure 1 – Observed bulk chemical variability across the investigated industrial black masses

Each point represents one independent industrial BM sample. Upstream-route categories are shown for descriptive comparison only. Battery chemistry and processing history are not independently controlled.

The bulk elemental inventories **vary and overlap** across the upstream-route categories. Pretreatment effects can therefore not be inferred from the bulk chemistry alone.

3 What does process-oriented characterisation add?

Phase & Reduction State

Table 1 – Simplified phase and reduction state matrix for selected feeds analysed with automated mineralogy

Feed	Oxidised CAM	Reduced CAM	Alloys	Metallic Al	Metallic Cu
M1	●	●	●	○	●
M3	●	●	●	●	●
V1	●	●	○	●	●
A1	●	○	○	●	●
TM1	●	●	●	○	●

● Dominant ● Partially present ○ Minor/Absent

Reduction states were inferred from phase occurrence and oxygen levels; electronic oxidation states were not directly measured. Additional qualitative SEM observations are shown below.

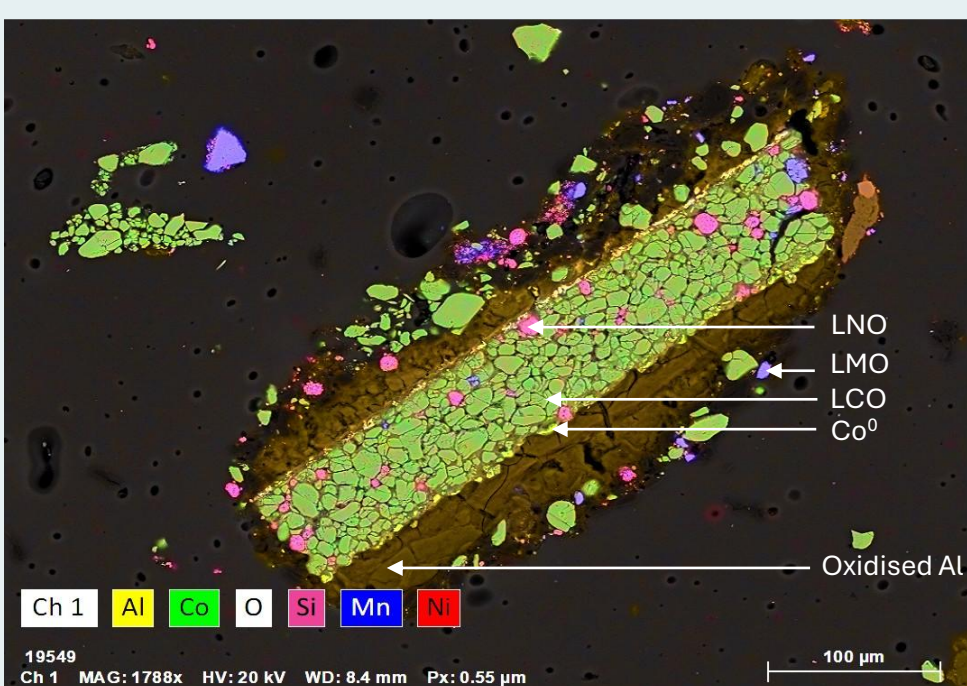


Figure 2 – Predominantly oxidised CAM with minor reduced Co occurrences coated on oxidised Al in M1 [1]

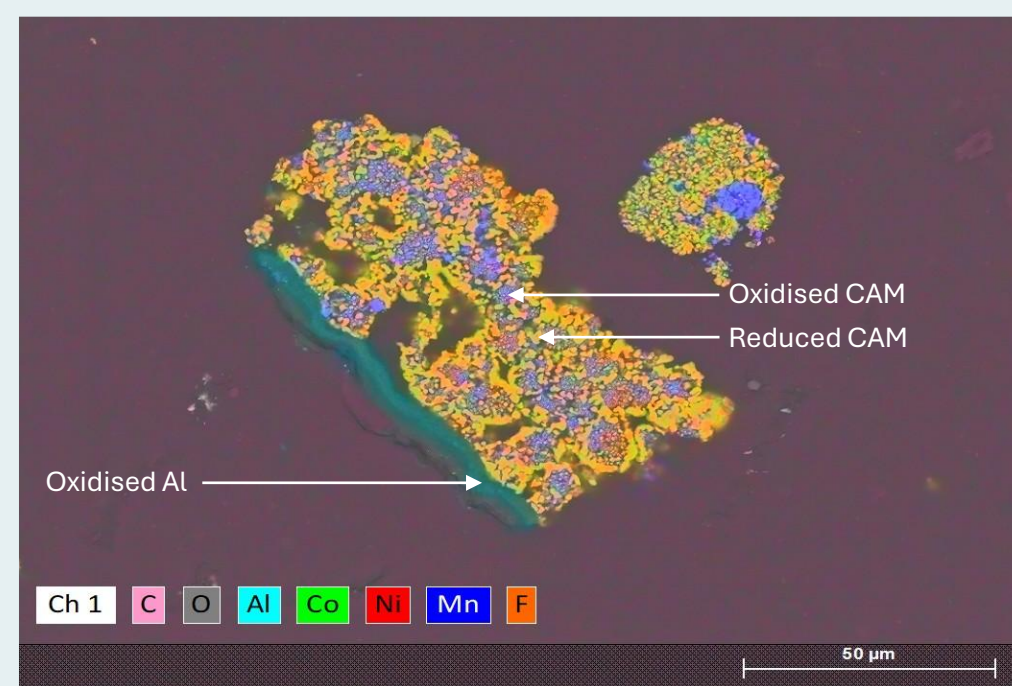


Figure 3 – Extensive CAM reduction around the core of preserved original oxidised CAM coated on oxidised Al in TM3

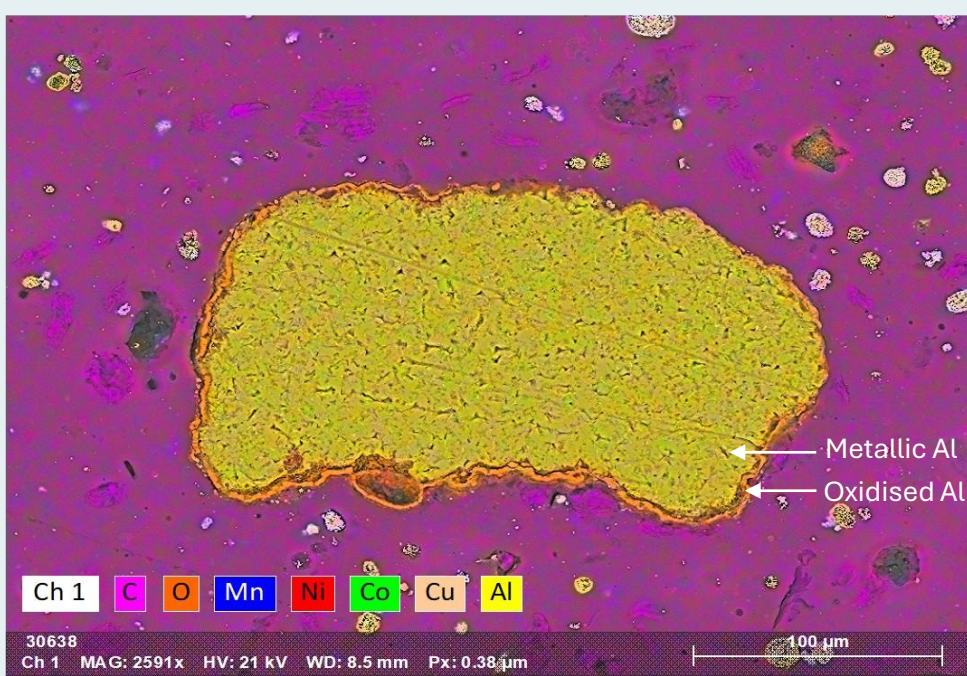


Figure 4 – Al surface oxidation in TM1

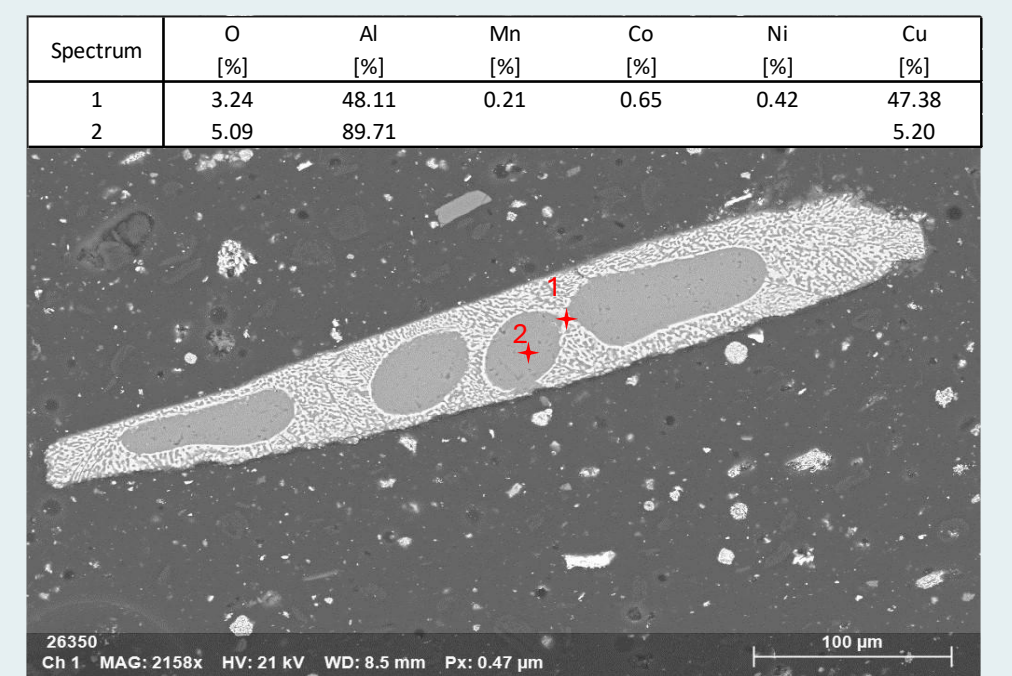


Figure 5 – Cu coating of Al and resulting alloying in TM2

Thermal history

Phase transformation /
reduction / alloying

External reduction
demand

Redox regime due to
alloy recalcitrancy

Thermal pretreatment can reshape the redox and phase state of the feed. Its downstream consequences depend on the transformation extent, itself depending on the pretreatment conditions (temperature, residence time, atmosphere conditions, etc).

Particle-scale state

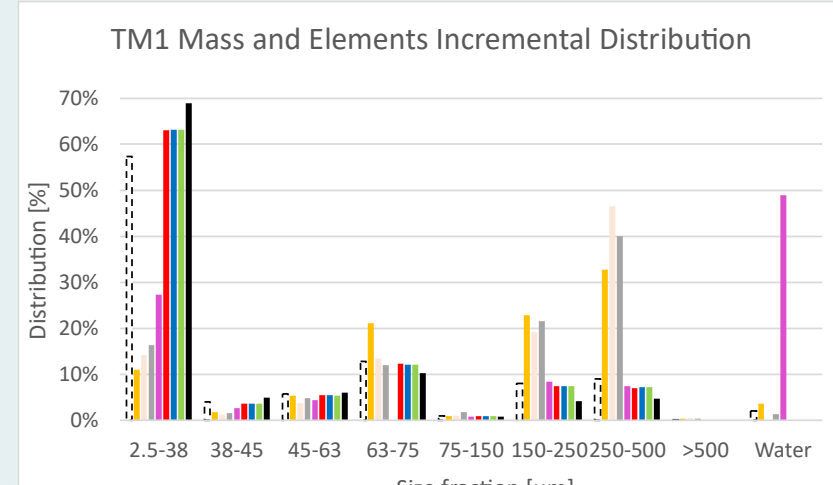
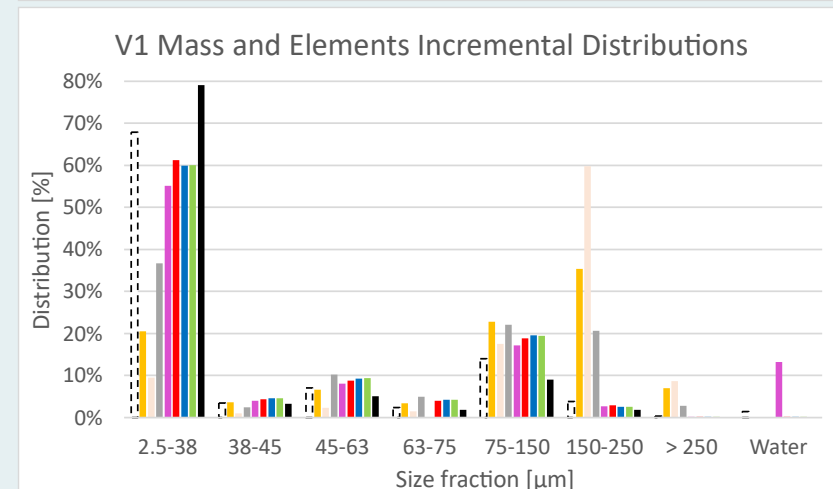
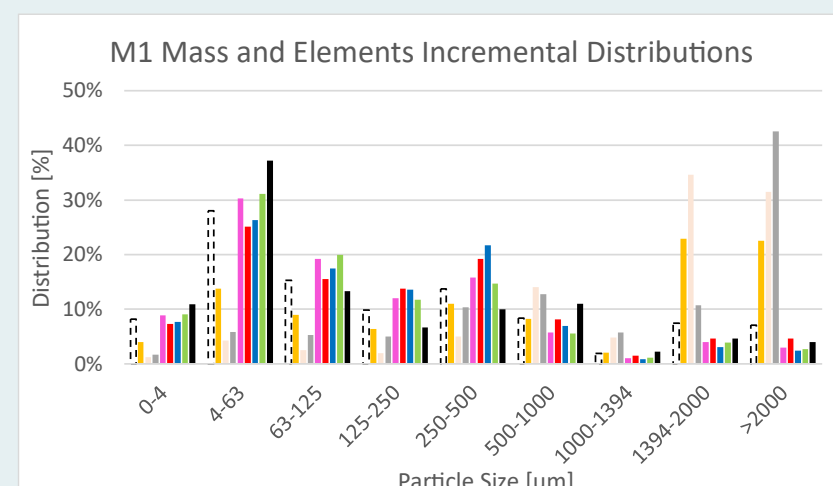


Figure 6 – M1, V1 and TM1 mass distributions and granulochemistries

M1 > 500 μm: 56% Al, 85% Cu, 11-14% AM. Up to 9% water-soluble Li.

V1 > 150 μm: 31% Al, 44% Cu, 2-4% AM. 19% water-soluble Li.

TM1 > 250 μm: 37% Al, 47% Cu, 7% AM. 49% water-soluble Li.

As particle size cut-offs differ between feeds, comparisons are made within each black mass sample rather than quantitatively between feeds.

However, the common trend is a coarser deportment of Al, Cu and Fe, and partial dissolution of Li, opening doors to (feed-specific) upstream processing improvements and early-stage lithium recovery.

4 Does it matter downstream?

Reduction State and External Redox Strategy

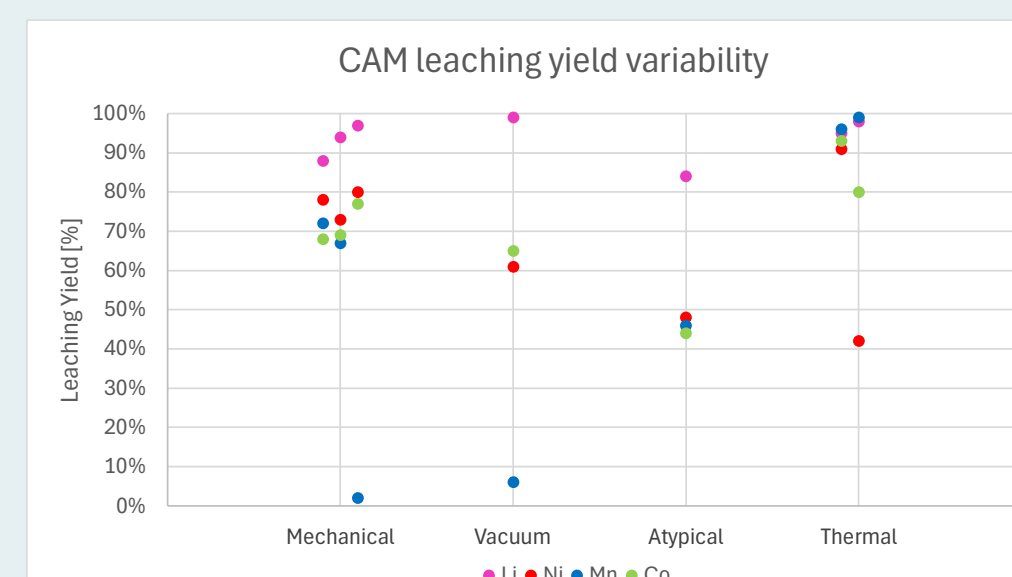


Figure 7 – CAM leaching yield variability across the investigated black masses in sulfuric acid (4h, 15% pulp density, ambient temperature, 2 mol H₂SO₄/mol eq. LCO*)

As feed chemistries and upstream histories differ between samples, this contrast should not be interpreted as an isolated causal effect of the thermal pretreatment.

* Moles of equivalent LCO; concept introduced for comparison purposes.

Thermally transformed feeds do not show a single redox response. While TM1 is responsive to a low external reduction supply, TM2 and TM3 require an oxidative redox regime under the studied conditions.

External **FeSO₄·7H₂O** addition to reach 95-100% CAM dissolution:

57 kg/t_{TM1} vs. 317 kg/t_{M1}

The lower external reducing agent need of the strongly reduced TM1 is consistent with the initially reduced phases.

Impurity Behaviour

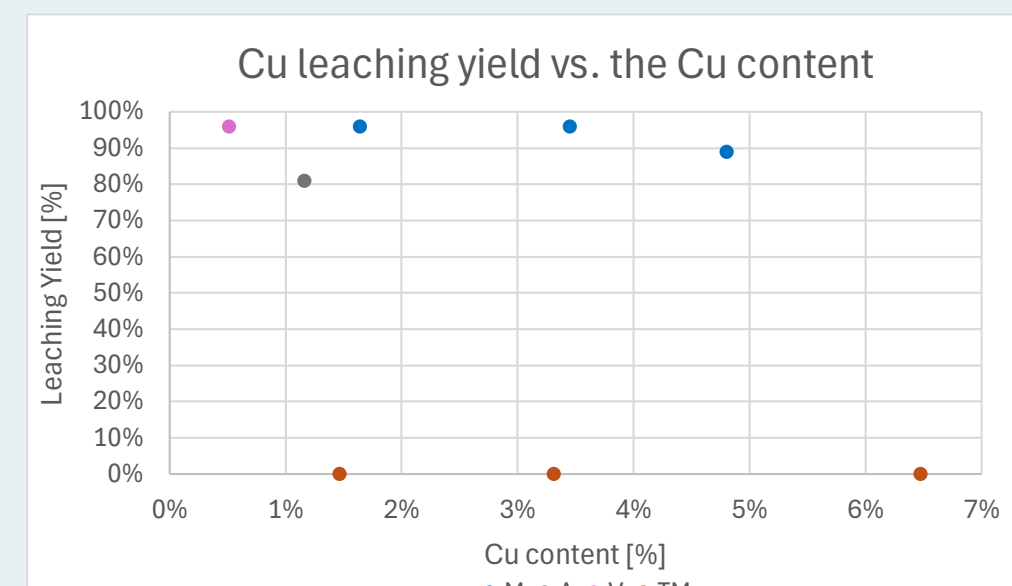


Figure 8 – Cu leaching yield variability across the investigated black masses

Bulk Cu (*in situ* reductant) content does not itself anticipate Cu dissolution; the same applies to Al. Phase occurrences (e.g. Ni(Co)Cu and AlCu alloys) and redox conditions also need to be considered

5 Towards a feed-adaptive hydrometallurgy

Bulk Chemistry

How much?

Li | Ni | Mn | Co
Al | Cu | Fe
C | F

Phase & Reduction State

In which form?

Oxidised
Reduced
Metallic | Alloyed

Particle State

Where and how distributed?

PSD | Deportment
Liberation
Association

Hydrometallurgical Response

Redox reagent demand
Transition metals extraction
Impurity dissolution
Residue behaviour

Feed-Adaptive Process Decisions

Physical upgrading
Feed blending
Redox strategy
Impurity management
Purification strategy

Figure 9 – Candidate descriptors for a process-oriented characterisation of black masses in view of a circular feed-adaptive hydrometallurgy

The next step is to identify the minimum combination of feed descriptors and their units to anticipate the downstream response under standardised hydrometallurgical conditions.

How (predictive) process-oriented characterisation could support circular hydrometallurgy:

- Avoidance of systematic reagent excess
- Improvement of impurity management
- Integration of physical pretreatment with the downstream hydrometallurgical processing

Take-Home Messages

Bulk chemistry is necessary but incomplete

Industrial black masses display broad and overlapping elemental compositions while upstream-route effects cannot be isolated from bulk assays alone.

Phase and particle state add process-relevant information

Phase occurrence, reduction state and particle deportment reveal material differences that may influence reagent demand and impurity behaviour.

No single measured descriptor explained all observed responses

The current dataset therefore suggests that a combination of phase and particle-scale descriptors may be required to anticipate the hydrometallurgical behaviour.

References: Vanderbruggen et al. 2021 (phase & particle characterisation) | Dadé et al. 2022 (industrial black masses variability & automated mineralogy) | Partinen et al. 2024 (intrinsic metallic reductants & leaching) | [1] Batutiako 2021 (Unpublished Master's thesis on black mass reductive leaching). AI use: spelling and grammar check and suggestions for content organisation and layout.

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