HYDROGEN-RELATED RESEARCH IN PYROMETALLURGY

Hydrogen breakfast meeting on 11.10.2023

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Research Group – Pyrometallurgy

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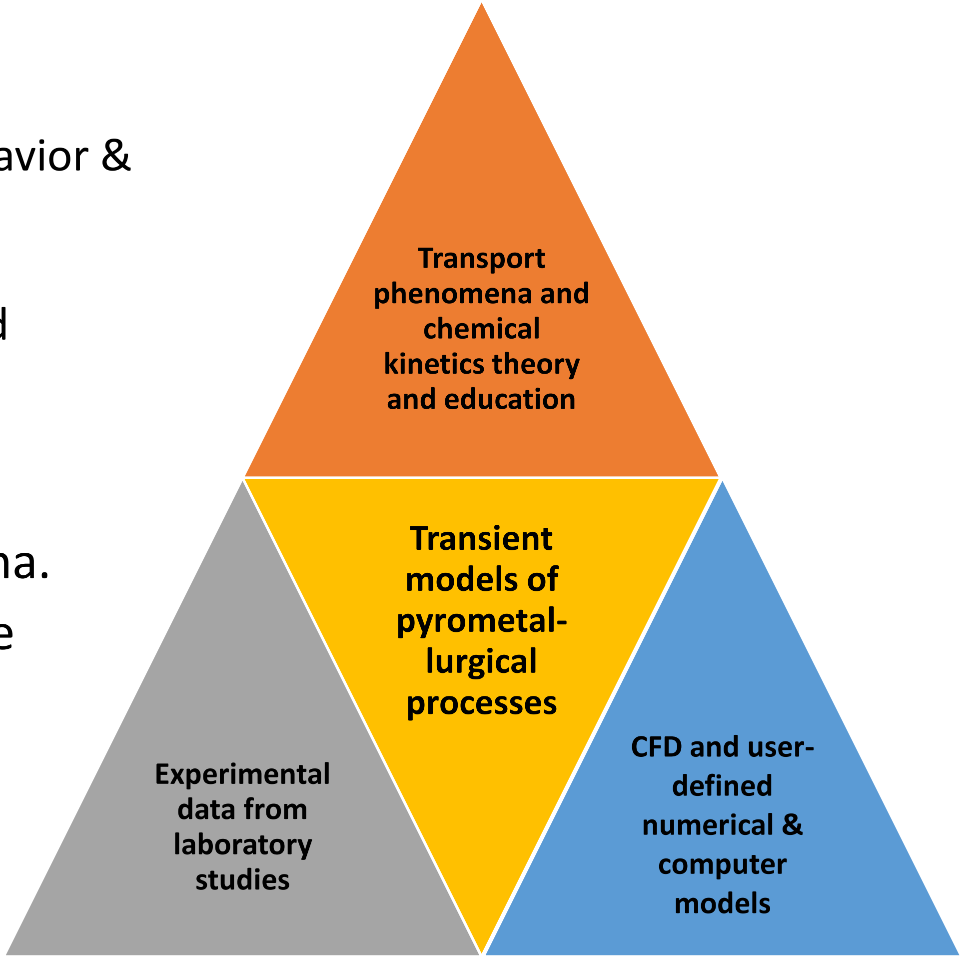
Research focus

- **Experimental investigation** of time-dependent (trace) element behavior & distribution in metallurgical melts.
- **Computer simulation** of time-dependent transport phenomena and chemical kinetics in high temperature metallurgical processes.
- **Focus areas:**
  - Metallurgical processes, reactions and transport phenomena.
  - Sustainable production and use of materials from low grade and complex primary and secondary resources.
- Research group:
  1 senior scientist, 1 staff scientist, 2 post-docs, 5-10 PhD students
  3-8 MSc students/year, 2 research assistants (part time)



Research works related to hydrogen as a reductant

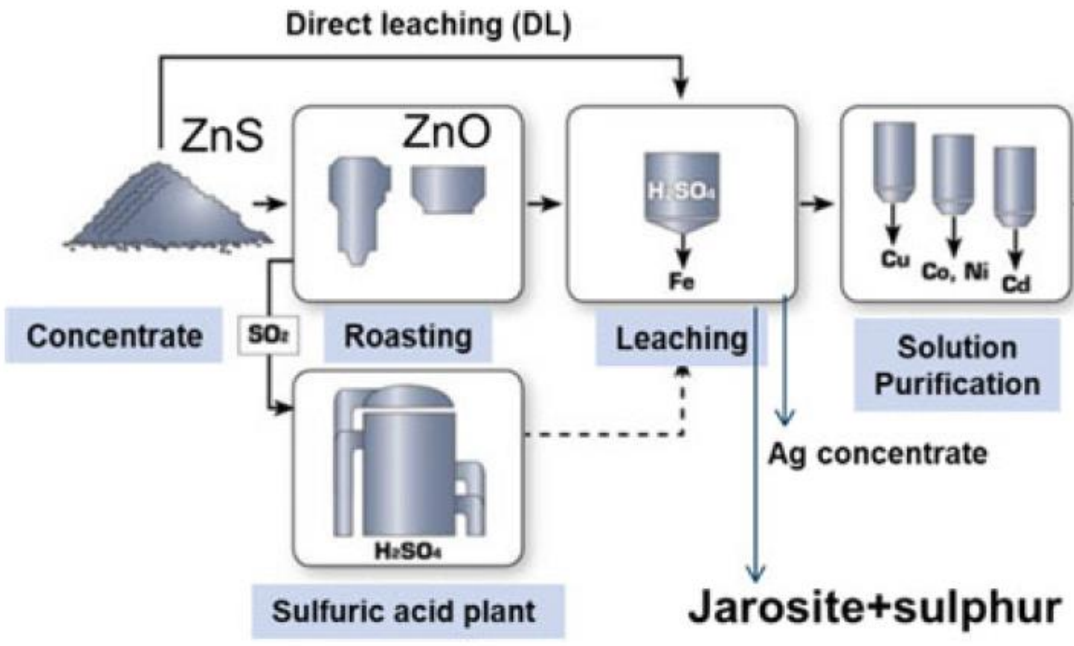
- Hydrogen as carbon-free reducing agent in jarosite processing (Desmond Attah-Kyei, collaboration with Prof. Daniel Lindberg's group)
- Hydrogen blowing for Ni/Cu-slag reduction (Min Chen & Dmitry Sukhomlinov & Jani-Petteri Jylhä)

Planned studies:

- Hydrogen as a reductant in Ni-slag/battery scrap reduction (BatCircle-project, Mohazzam Saeed, collaboration with Prof. Rodrigo Serna's group)
- Hydrogen blowing in nickel slag reduction (ENICON-project, Fabiola Lasar, continuation of previous experiments)

What is jarosite?

Jarosite composition: Zn 2.9%, Pb 2.7%, Fe 15.2%, Ca 3.2%, S 31.7%, Si 2.0%, Na 1.6%, Cu 1.3%, As 0.7%, Al 0.6%, Cd 0.1% + small amounts of other valuable metals



= combined residue

Fig. 2 Boliden Kokkola roasting, leaching, electrowinning (RLE) flowsheet

Amount of combined residue in Kokkola: more than 6 million dry metric tonnes, 230 000 dmt/year increase. Classified as hazardous waste.

Fig. 3 Landfilled combined residue at Boliden Kokkola

Justin Salminen et al. Smelting Jarosite and Sulphur Residue in a Plasma Furnace. A. Siegmund et al. (eds.), PbZn 2020: 9th International Symposium on Lead and Zinc Processing, p. 391-403. The Minerals, Metals & Materials Series.

What have we done with jarosite previously?

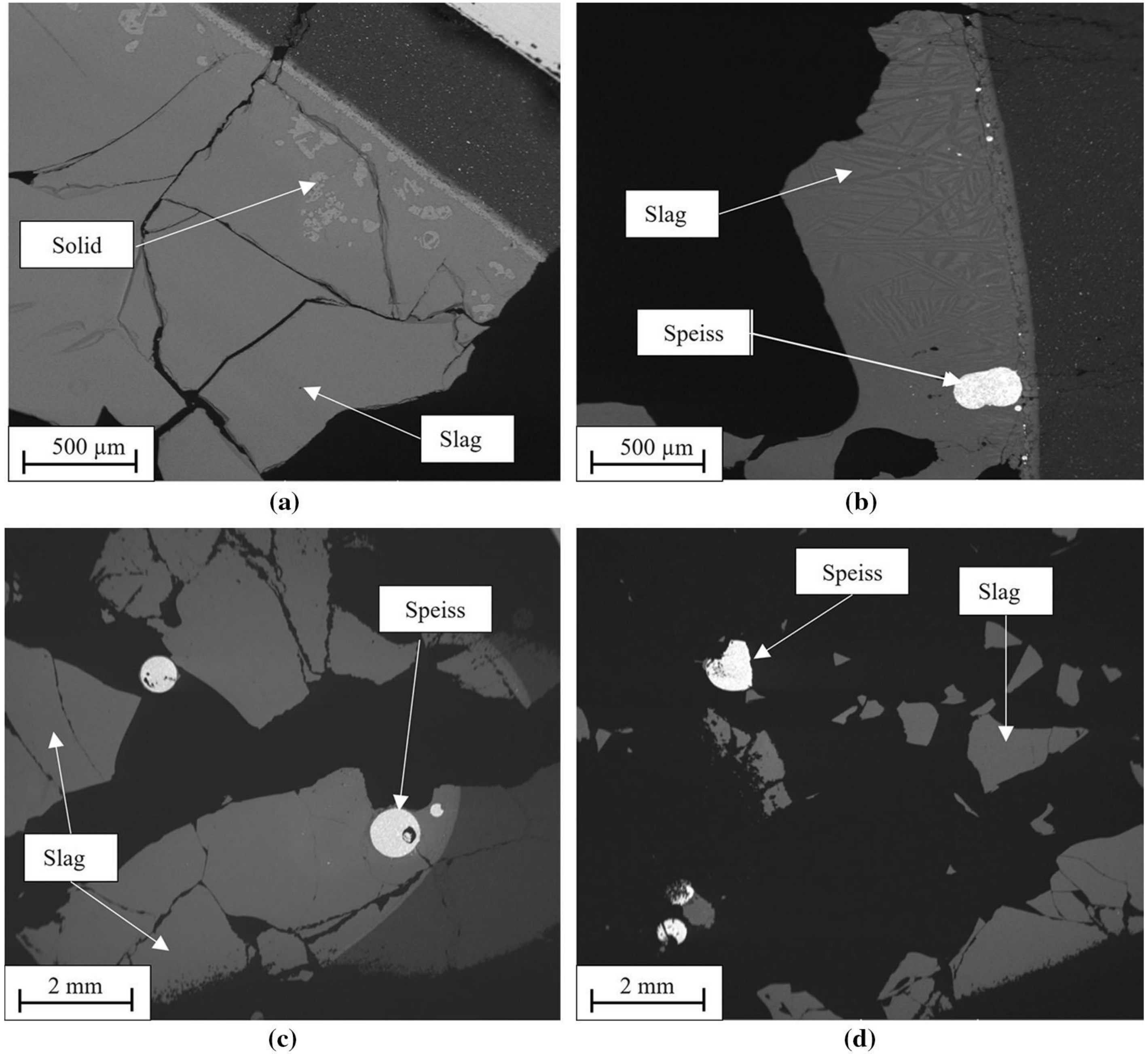
- The goal of high-temperature treatment is to get hazardous elements (to avoid being classified as hazardous waste) and valuable metals (economic benefits) either to volatilize or collect in metal phase

- CO-CO_2 gas mixture, coke and biochar have been studied as reductants earlier

- Hydrogen, if produced using green electricity, could be a sustainable reductant in industrial-scale processes

H_2 reduction of jarosite

- Temperature 1200-1300 °C
- Two-stage process: oxidation (O_2, 60 min)-reduction (N_2-20H_2, 5-20 min)
- Goal was for Pb and Zn to volatilize or deport to metal/speiss phase in order to produce a "clean" slag (not classified as hazardous waste)

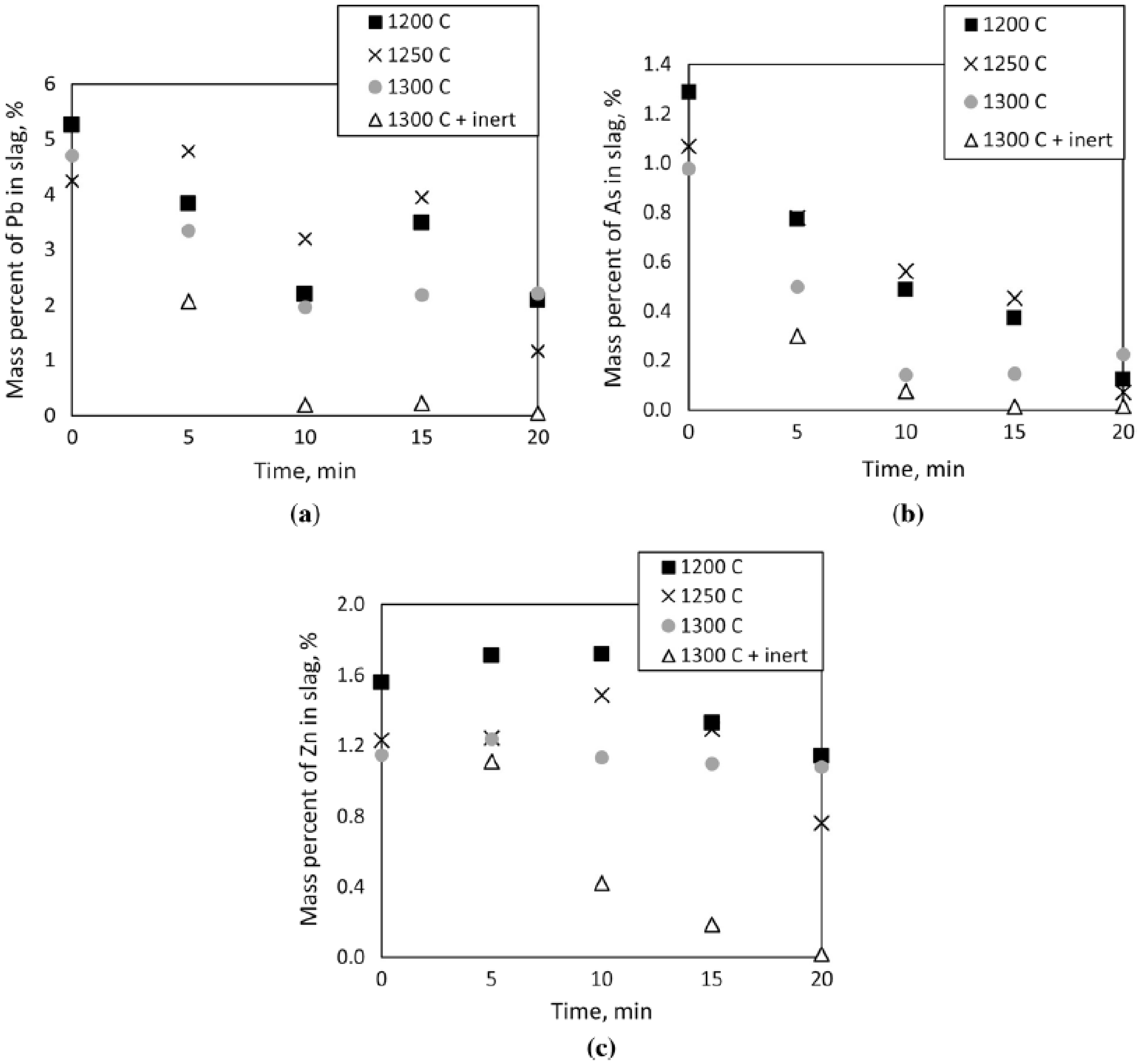


Micrographs of samples after (a) 5, (b) 10, (c) 15, (d) 20 minutes of H_2 reduction at 1300 °C.

Desmond Attah-Kyei et al. Hydrogen as Carbon-Free Reducing Agent in Non-ferrous Slag Fuming. Metallurgical & Materials Transactions B, 2022. Vol. 53, p. 3775-3792.

H_2 reduction of jarosite

- Concentrations of Pb, As and Zn in slag decrease as a function of increasing reduction time
- Additional 60 min at 1300 °C in inert conditions improved the slag cleaning significantly



Concentrations of Pb (a), As (b) and Zn (c) in slag after H_2 reduction.

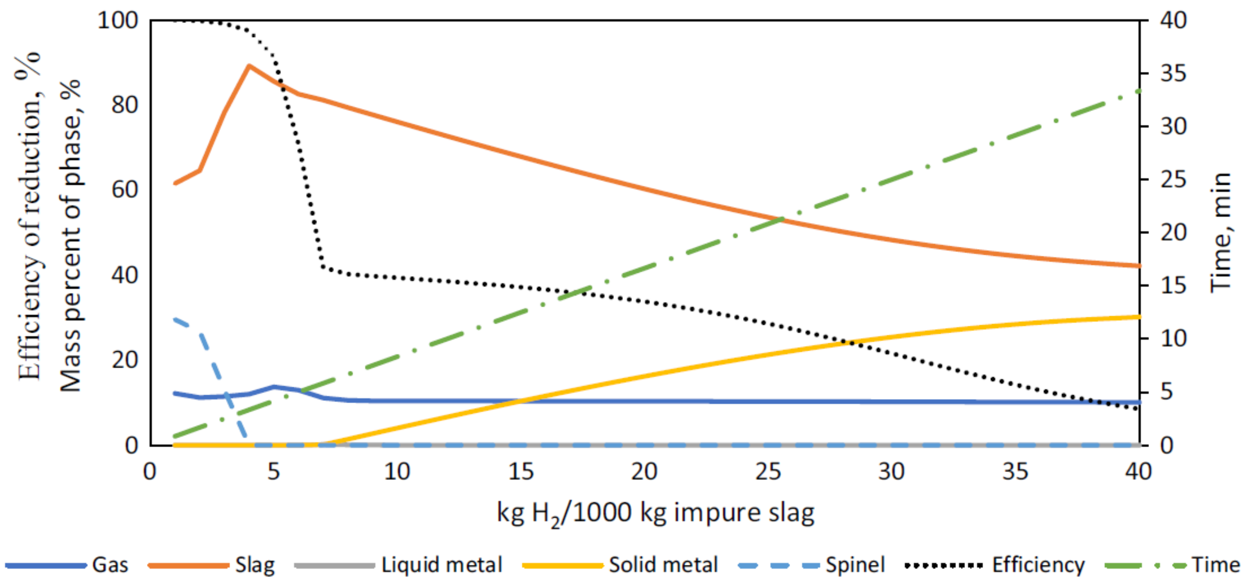
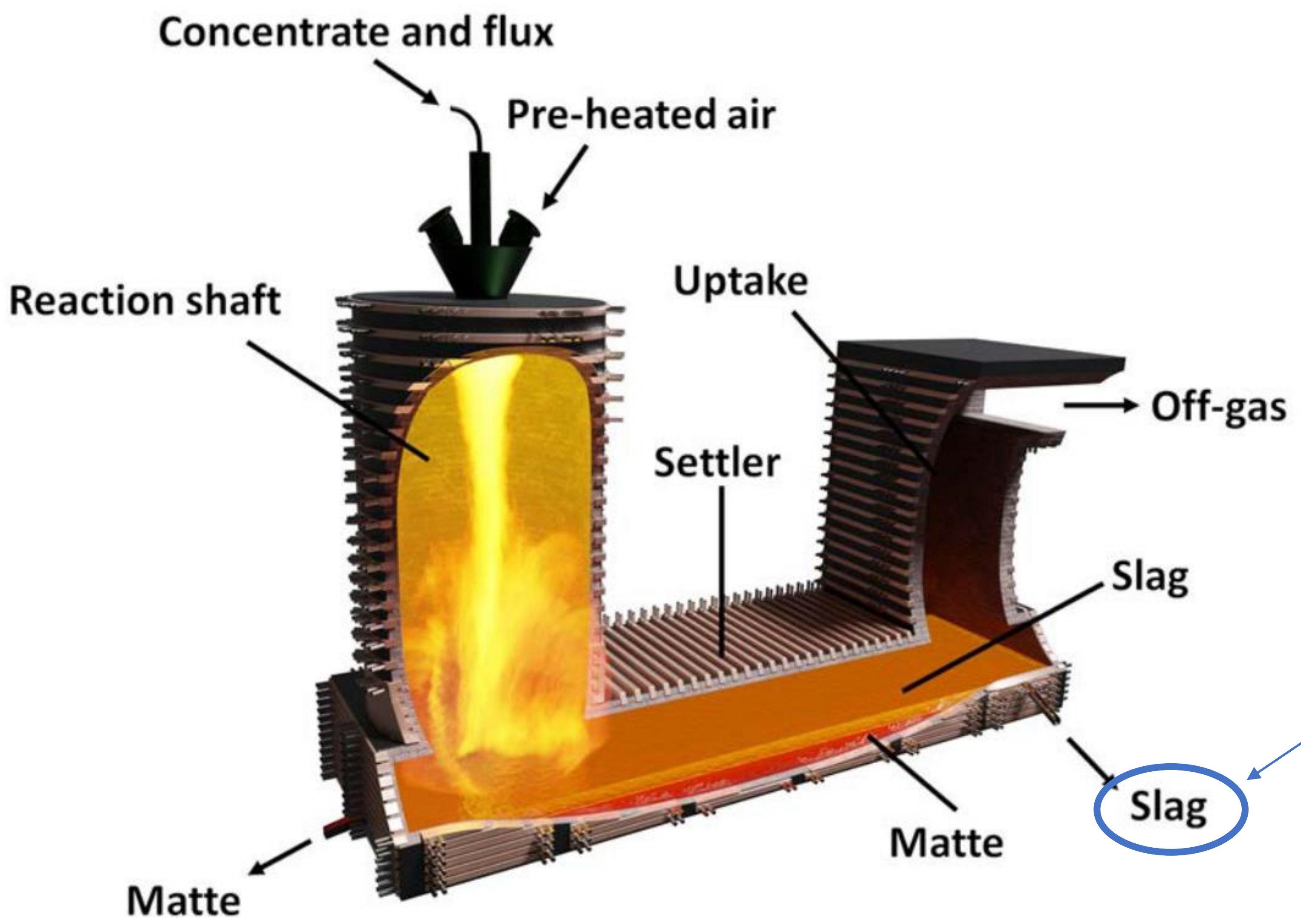


Fig. 14—Mass of phases obtained from impure slag reduction at 1300 °C with 20 vol pct H_2 predicted by FactSage.

Where does nickel / copper slag come from?



Contains still some Ni, Cu and Co, processed in a separate furnace (reduction of valuable metal oxides)

J.-P. Jylhä et al. Computational approaches for studying slag-matte interactions in the Flash Smelting Furnace (FSF) settler. Processes 2020, 8(4), 485

H_2 blowing for Ni-slag reduction

- Current industrial practice is to reduce Ni-slag using metallurgical coke
- In this work, the goal was to test hydrogen as a reductant instead of coke

Surface blowing experiments with H_2

m(slag) = 15 g
total gas flow rate (H_2+Ar) = 100 ml/min

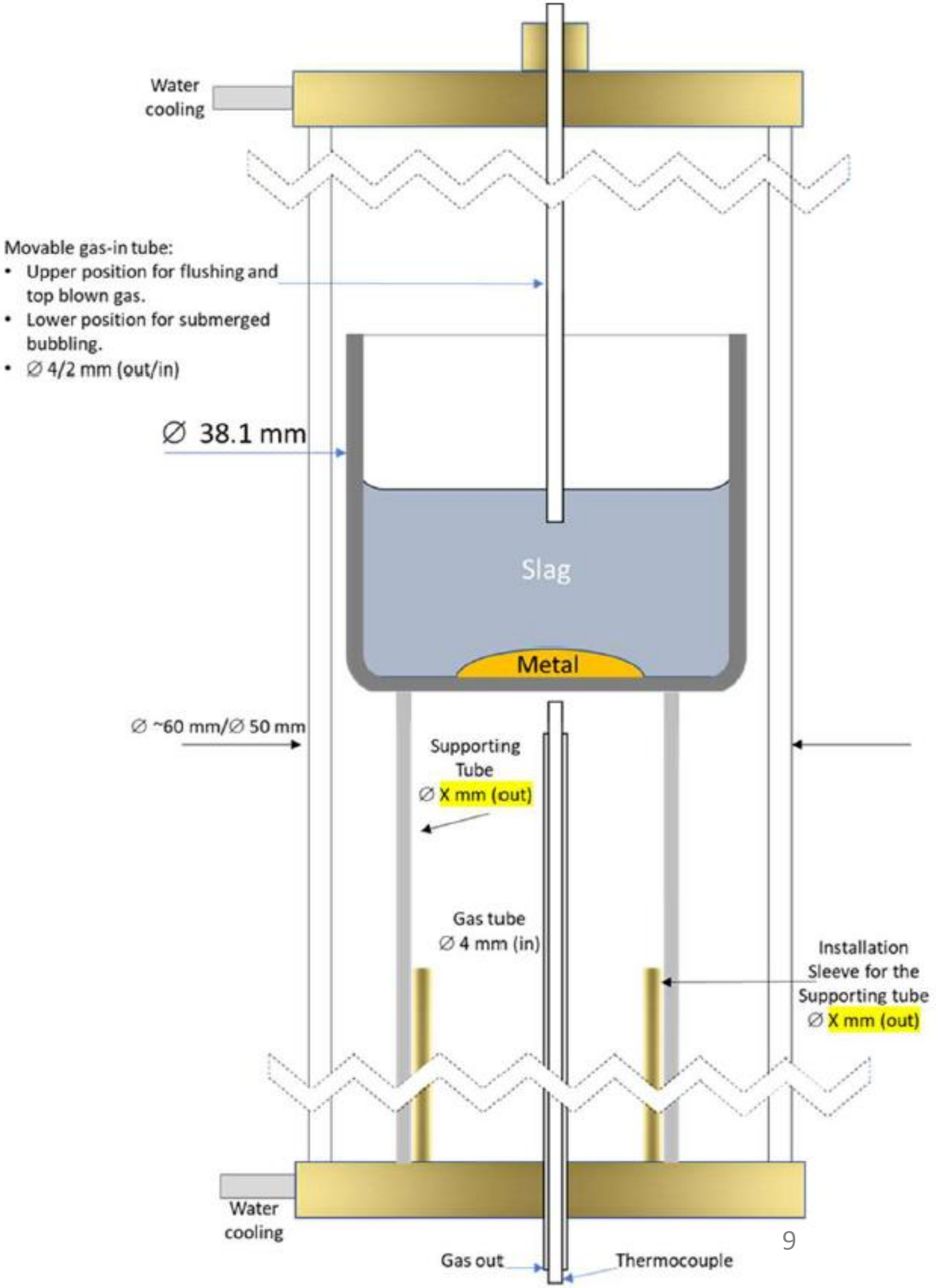
	Reduction time, mins			
H_2 concentration, vol%	30	60	120	360
10	A8	A2, A9	A10	A4
25		A3, A7		
50		A5, A6		

Bubbling experiments with H_2

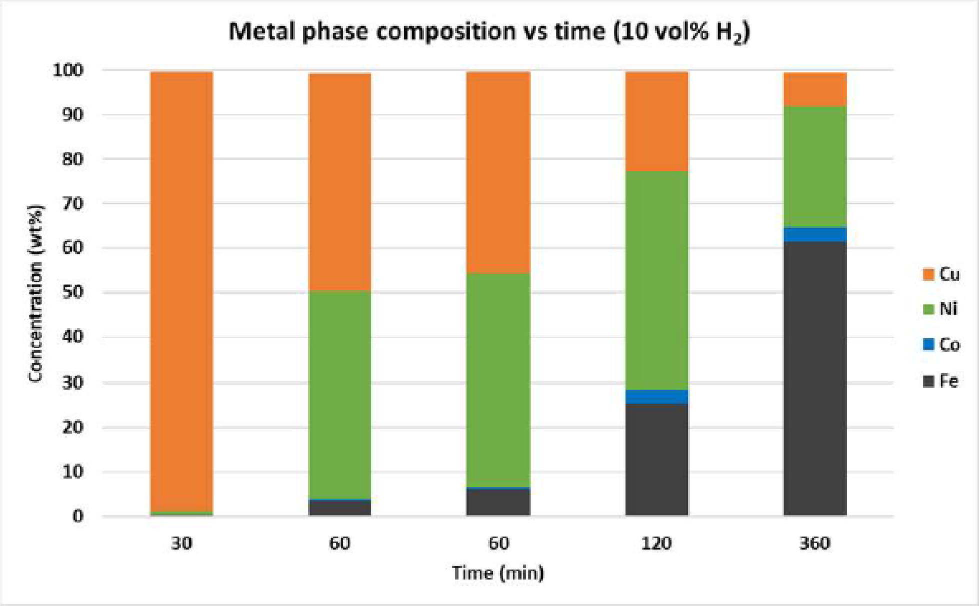
m(slag) = 15 g
total gas flow rate (H_2+Ar) = 77 ml/min

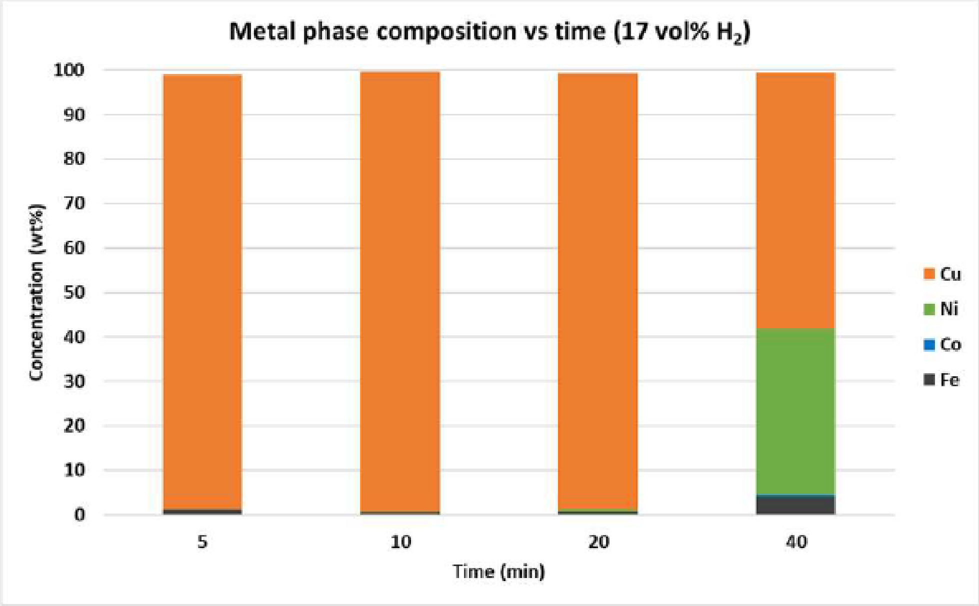
	Reduction time, mins			
H_2 concentration, vol%	5	10	20	40
17	C1	C2	C3	C4

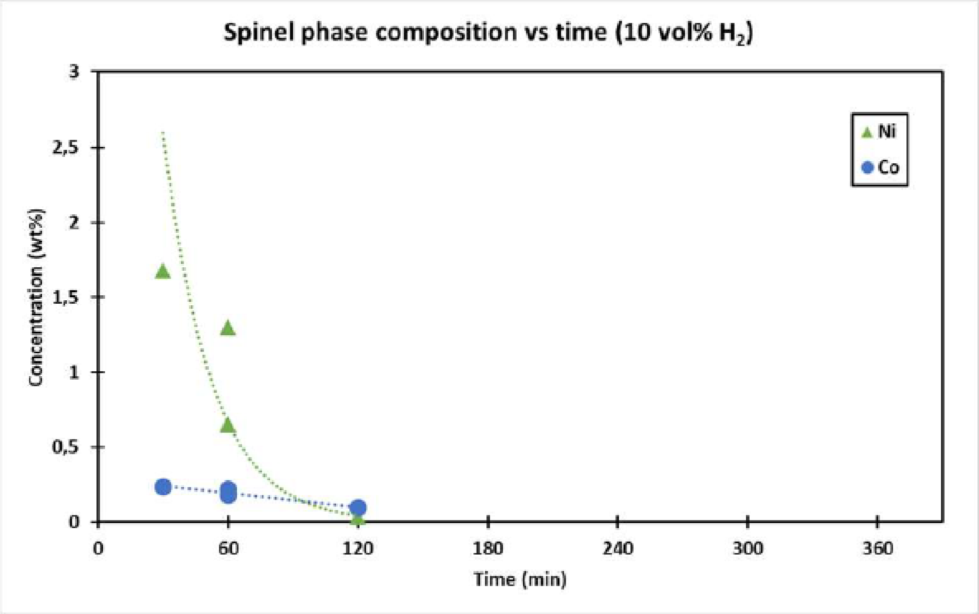
Temperature 1400 °C

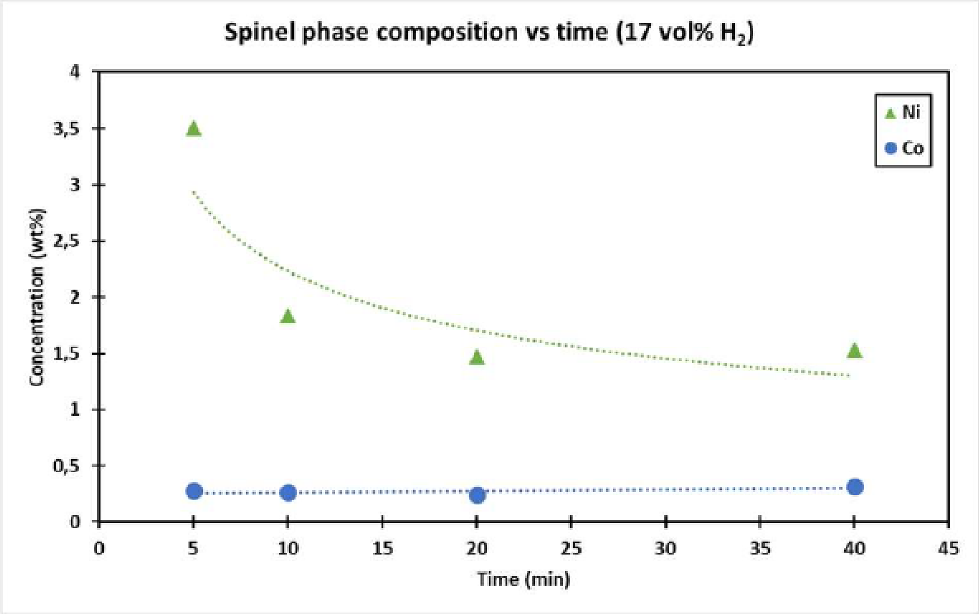


Surface blowing and bubbling comparison

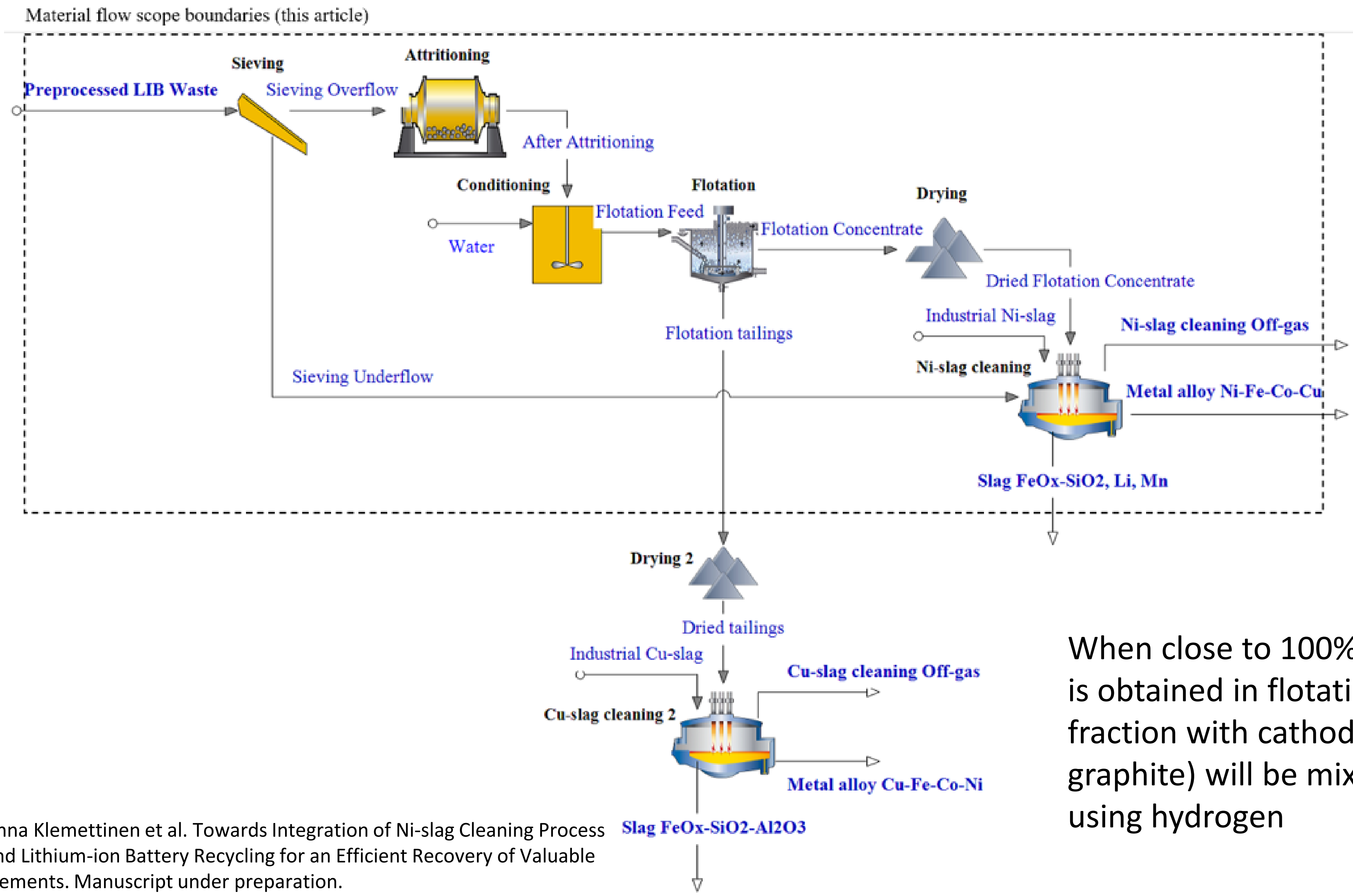








Integrating mechanical processing and pyrometallurgy



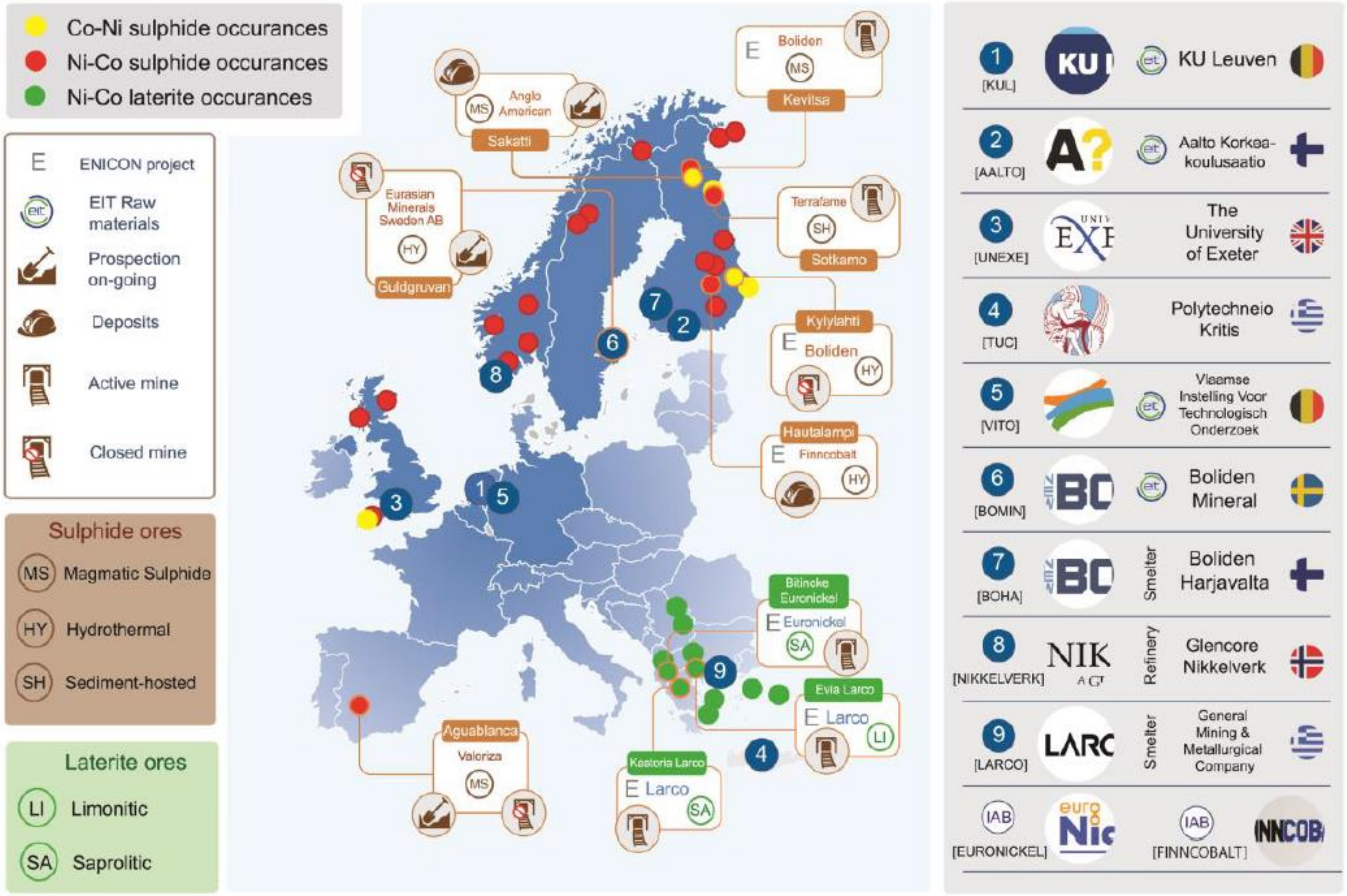
Previously done: lithium-ion battery scrap was first treated using flotation (separating cathode active materials from Cu, Al and graphite), followed by mixing cathode material fraction with Ni-slag and melting it at 1350 °C (reductant is graphite that was left in the cathode material fraction)

When close to 100% efficient graphite separation is obtained in flotation stage, the flotation fraction with cathode active materials (no graphite) will be mixed with Ni-slag and reduced using hydrogen

Anna Klemettinen et al. Towards Integration of Ni-slag Cleaning Process and Lithium-ion Battery Recycling for an Efficient Recovery of Valuable Elements. Manuscript under preparation.

ENICON-project

Sustainable processing of Europe's low grade sulfidic and lateritic Ni/Co ores and tailings into battery grade metals



Locations of Ni/Co sulfide & laterite deposits and mines, as well as ENICON consortium overview

ENICON-project goals related to hydrogen

- Work package 2, objective 3: To develop a H_2-based, carbon-neutral smelting/converting process for Ni/Co-sulfide concentrates
  - Minimum target: H_2 replaces cokes achieving same Ni/Co yield. Ideal result: additional 10% increase in Ni/Co yield.

  - **Hydrogen reduction in the Ni/Co-sulfide pyro-route.** Sulfide smelting slags are cleaned in electric arc furnaces with coke, resulting in significant CO_2 emissions. The recovery rates for valuable metals (Ni, Co, Cu) need to be improved. Gaseous reductants have reducing power, but due to an abundance of coke and problems storing gases, they have not been studied. ENICON will investigate how reductants like hydrogen can be used to recover Ni + Co in sulfide smelting-slag reduction. The hypothesis is that the reaction kinetics can be increased by mixing the molten slag with gaseous reductants. The result would be more efficient Ni and Co reduction to the metal.
  - The kinetics of carbon-free reduction will be investigated with reduction phenomena on a lab scale, followed with further tests by BOHA on a larger scale, to confirm the commercial possibilities.

Thank you!

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